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The chemistry of nitroxide radicals in the molecular design of magnets

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Abstract. The state of the art of the chemistry of nitroxide radicals promising for the design of molecular magnets is considered. The bibliography includes 303 references.

I. Introduction

The development of civilization is inconceivable without wide use of magnetic materials. Even not long ago these were mainly metals (for example, Fe, Co, Ni, Gd), alloys of transition metals with one another or with lanthanides, oxides and other binary or ternary compounds of transition elements.[1–3] However, the growth of technology pressed for the development of new magnetically active materials with new, previously unknown combinations of physical properties.[4] This gave rise to new trends of fundamental research, in particular, in the field of molecular magnetism and spintronics.[5–8]

An intriguing idea of molecular magnetism is to create new types of magnetically active compounds saturated with organic components on the basis of approaches of synthetic chemistry. This would give magnets with properties typical of organic compounds: low density, elasticity, solubility in organic solvents, transparency over a broad range of electromagnetic spectrum, high resistance to electric current and biocompatibility.

Development of the studies in this area soon revealed the specific requirements to the organic components. To ensure that the introduced organic fragments do not turn out to be mere diamagnetic insulators between the paramagnetic centres (PMC) of metals, they should be magnetically active compounds, in particular, organic paramagnets — kinetically stable organic radicals [9] whose structure is favourable for 'conducting' the spin density of the unpaired electron. The crucial role belongs here to stable nitroxide radicals (NR).[10,11] A large body of knowledge has now been accumulated concerning the targeted development of methods for the synthesis of NR with favourable structure for the design of magnetically active multispin systems. This knowledge rapidly increases, these NR being the subjects of publications in journals of quite different subject matters. The need to generalize and systematically survey this knowledge stimulated the writing of this review.

In the design of molecular magnets, so-called limiting case is possible where metals or metal ions are totally absent in the solid phase, *i.e.*, the whole phase is composed of organic components. These are still rare but highly unusual examples of organic magnets. The first part of this review discusses data concerning the design of such purely organic molecular magnets on the basis of mono- and polynitroxides.

The NR specially synthesized for the molecular design of magnets represent an extensive class of compounds. A greater part of the review is devoted to them. We intended to emphasize an important structural feature of the discussed NR molecules: conjugation of the $>N\dot{-}O$ group with the unsaturated fragment. This is the goal of researchers working in this field because for molecular design of heterospin magnets, this conjugation promotes the existence of highly effective, *i.e.*, high-energy, exchange interactions between the unpaired electrons of the PMC. However, this situation is not trivial from the synthetic standpoint and requires the development of special methods and practices. For this reason, the attention here is focused on essential details of the chemical experiment, which either emphasize the key feature of the synthetic procedure or are important for reliable reproduction of the synthesis.

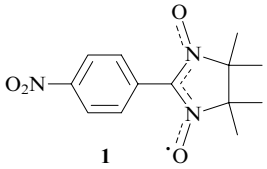
Note that despite the specific ideology of this review, *viz.*, development of methods for the synthesis of NR promising for the molecular design of magnets, it may also be useful for the researchers engaged in classical nitroxide chemistry, because more than 15 years have passed since the publication of the last large review [11] in this field.

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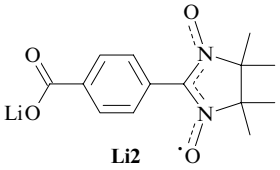
II. Molecular magnets based on nitroxides

The first organic ferromagnet, the orthorhombic modification (β-phase) of 4,4,5,5-tetramethyl-2-(4-nitrophenyl)-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide (**1**), underwent the transition to the ferromagnetic state below the Curie temperature (T_C) equal to 0.60 K.[12–14] Its triclinic modification (γ-phase) behaved as a quasi-1D-system where antiferromagnetic transition took place below the Neel temperature (T_N) equal to 0.65 K.[15,16] In the α- and δ-phases of **1**, no magnetic phase transition was found at all. Under pressure, the β-phase of **1** transformed from ferromagnetic to 2D-antiferromagnetic state. On the whole, the results of investigation of radical **1** have become a vivid example of the effect of polymorphism on the intermolecular exchange interactions, which predetermine the macroscopic magnetic properties of NR. They also show that elucidation of the magnetic-structure relationships is an important part of investigations carried out in molecular magnetism.



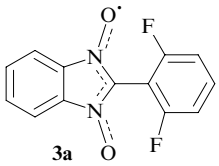
1

Systematic research of the magnetic-structure relationships inherent in the polymorphs of **1** actually laid the grounds for the search of ferromagnets among the kinetically stable organic spin-labelled compounds. Currently, development of the foundations of the crystal design of magnetically active compounds of this type is in progress. An important component is accumulation and analysis of the data about the NR that have ferromagnetic exchange in solid phases. Systematic study of the magnetic-structure relationships carried out by Togashi *et al.*[17] for crystals of 165 derivatives of 4-arylmethylideneamino-2,2,6,6-tetramethylpiperidin-1-oxyls revealed the geometry of the contacts of the $>N\dot{-}O$ group with the aromatic ring π-system that is favourable for the ferromagnetic intermolecular exchange. However, in 2,2,6,6-tetramethylpiperidin-1-oxyls and related nitroxides with isolated $>N\dot{-}O$ group, the energy of exchange interaction is very low (~0.01 K) due to low spin density at peripheral atoms. A considerable increase in the efficiency of exchange channels can be attained by using NR with spin density delocalization. For example, the crystals of **Li2**·0.5 MeOH are composed of dimers in which ferromagnetic exchange interactions with $2J/k = 31.8$ K, where J/k is the exchange interaction constant, take place. Crystal structure analysis demonstrated that in the dimers $\{\mathbf{Li2}\}_2$ the oxygen atom of the paramagnetic fragment of one molecule is proximate to the C(2) atom of another molecule. This results in the interaction of positive spin density of great amplitude on one NR with a small negative spin density on C(2) of the neighbouring NR, which is responsible for the ferromagnetic aligning of magnetic moments in the exchange dimer.[18]



Li2

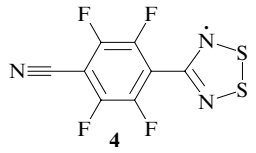
The replacement of the $-CMe_2-CMe_2-$ fragment in the NR of type **1** by a 1,2-phenylene fragment affords benzoimidazol-1-oxyl 3-oxide **3**. The planar structure of NR of this structural type in combination with effective spin density delocalization promotes the formation of channels in the crystal ensuring rather strong both antiferromagnetic (AF) and ferromagnetic interactions between unpaired electrons. The peak value of ferromagnetic exchange energy $J/k = 66$ K was recorded in one of the crystal modifications of benzoimidazol-1-oxyl 3-oxide with 2,6-difluorophenyl substituent in position 2 (**3a**).[19]



3a

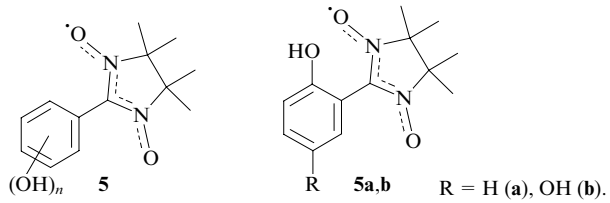
Systematic studies of the magnetic properties of nitroxides may involve analysis of numerous variants of exchange interactions for small groups or separate representatives of NR.[20–25] The consistent accumulation of the data on the ways of formation of channels providing the ferromagnetic exchange in the solid phase and their quantum chemical investigation[26–28] are favourable for targeted search for organic ferromagnets. The results of quantum chemical studies aimed at elucidation of the origin of ferromagnetic exchange in solid NR are of considerable value also for the understanding of exchange interactions in complex heterospin systems based on compounds of paramagnetic transition metal ions with organic radicals.[29,30]

Below T_N, the formation of spontaneous magnetic moment is also possible due to disalignment of various sublattices of the NR molecules. Since the angle between the vectors of the magnetic moments of sublattices normally does not exceed several degrees, a slight spontaneous magnetization, *i.e.*, weak ferromagnetism, appears in the transverse direction. This was identified for a number of 2,2,6,6-tetramethylpiperidin-1-oxyl and 4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide derivatives and was characterized by low T_N values.[31,32] Low T_N values in the molecular crystals are due to low energy of exchange interactions between the unpaired electrons of the PMC located at considerable distances from one another. This points to one of the possible ways of increasing the critical temperature: in order to increase the energy of intermolecular interaction in the organic paramagnetic crystals, it is desirable to avoid bulky substituents such as $-Bu^t$ or $>CMe_2$, *i.e.*, 'planar' NR molecules should better be used. These 'planar' radicals may attain a closer packing in the crystal and, hence, a larger concentration of unpaired electrons per unit volume and more effective interactions are possible. Within the framework of this approach, indeed, an increase in T_N was attained; for example, for 1,3,5-triphenyl-6-oxoverdazyl this value was 5.0 K. The highest T_N value in the series of 'planar' organic magnets was found for the β-phase of 4-(4-cyano-2,3,5,6-tetrafluorophenyl)-3*H*-1,2,3,5-dithiadiazolyl (**4**), which undergoes a magnetic phase transition to a weak ferromagnetic state at $T < 35.5$ K and ambient pressure.[33–35] As the pressure increases to $\sim 16 \times 10^8$ Pa, the Néel temperature increases to 65 K.



4

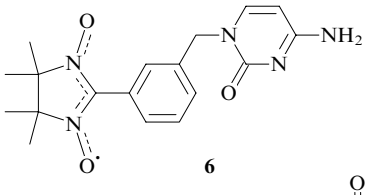
Exchange interaction channels between the PMC may also arise upon the formation of intermolecular hydrogen bonds between the oxygen atoms of the O$\dot{-}$N$<$ and OH groups of neighbouring molecules. For example, these H-bonds are formed in the crystals of nitronyl nitroxides **5**. Depending on the number and positions of the OH groups, primary zero-, one-, two-, or three-dimensional exchange-bound clusters are formed, which accounts for the diversity of the magnetic properties of radicals of family **5**,[36–39] in particular, their capability for magnetic ordering. The *o*-hydroxyphenyl-substituted isomer **5a** (T_C = 0.45 K) and 2,5-dihydroxyphenyl-substituted nitronyl nitroxide **5b** (T_C = 0.5 K)[40,41] became the first examples of organic ferromagnets whose primary structure is specified by intermolecular H-bonds.



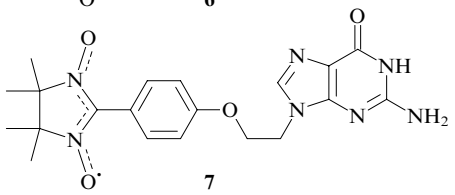
5 **5a,b** R = H (**a**), OH (**b**).

The discovery of these organic ferromagnets stimulated the search and implementation of diverse ways of associating nitroxides with H-bonds.[42–45] The magnetic-structure relationships inherent in 2-(1,3-dihydroxy-2-methylpropan-2-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide (the common name for the heterocycle is 2-imidazolin-1-oxyl 3-oxide) were studied.[46] This gave molecular complexes of 2-phenyl-substituted nitronyl nitroxide with $PhB(OH)_2$ (1 : 1), in which ferromagnetic interaction with $2J/k \approx 1.3$ K takes place due to the formation of NO···HO−B−OH···ON chains.[47] The expectation for the formation of such chains in the 4-$(OH)_2BC_6H_4$-substituted nitronyl nitroxide did not come true; one oxygen atom of the O$\dot{-}$N−C=N→O fragment was not involved in the H-bonding.[48] The ferromagnetic 1D-chains with $2J/k \approx 6.7$ K present in the solid phase of the complex of 2-(4-hydroxyphenyl)imidazoline nitronyl nitroxide with 1,2-bis(diphenylphosphinoyl)ethane are also formed through H-bonding.[49]

Various hetaryl-substituted 2-imidazolin-1-oxyl 3-oxides capable of H-bonding were synthesized. Particular attention was attracted to heterocyclic substituents that could provide linear association of a paramagnetic molecule. For example, a broad range of spin-labelled imidazoles and their annulated derivatives,[50–53] triazoles[54,55] and azaindole isomers[56,57] were prepared. The solid phases of these compounds demonstrate diverse architecture and magnetic properties. An attempt was made to use the principle of formation of the DNA double helix for preorganization of PMC. For this purpose, several spin-labelled heterocyclic residues of nucleic acids were prepared and magnetic-structure relationships were studied for them. It was shown that during crystallization, the heterocyclic base in uracil-,[58] cytosine- (compound **6**)[59] and guanine-substituted (compound **7**)[60] 2-imidazolin-1-oxyl 3-oxides serves as the key structuring unit.



6



7

Weak intermolecular hydrogen bonds C−H···O or C−H···N can also dictate the packing motif for paramagnetic molecules in the crystal. Examples of such compounds are spin-labelled carborane **8** (Ref. 61) and imidazolin-1-oxyl **9** with a terminal acetylene substituent in position 2 (Fig. 1).[62]

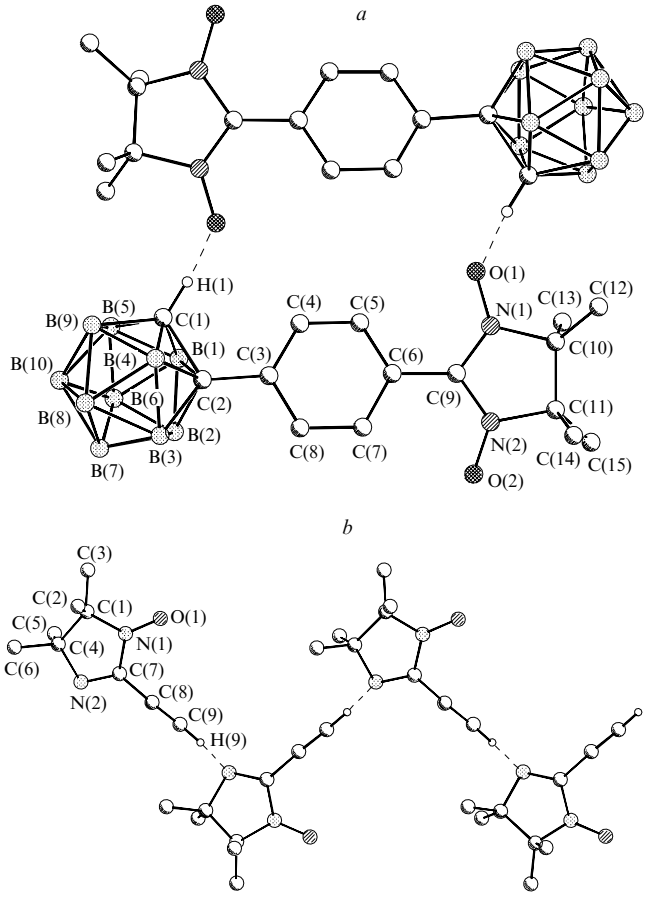
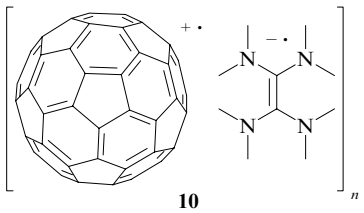


Figure 1. Hydrogen bonds in the structures of nitroxides **8** (*a*) and **9** (*b*).

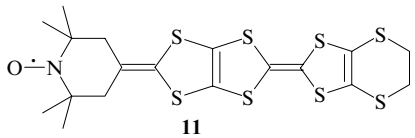
Apart from H-bonding, electron transfer from a reductant to oxidant is yet another effective tool in the design of spin clusters. As shown by McConnel,[63] in these compounds, ferromagnetic exchange between the unpaired elec-

trons of the PMC can occur under certain conditions. Historically, the first example of this type of ferromagnet described by Miller and Epstein[64] was $[Fe^{III}(C_5Me_5)_2]^{+\bullet}.[TCNE]^{-\bullet}$ (TCNE is tetracyanoethylene), which had a positive Curie–Weiss constant, $\theta = 30$ K and $T_C = 4.8$ K. This was followed by discovery of a lot of diverse compounds capable of magnetic ordering. Examples include well-known tetracyanoethylene vanadium complex $V^{II}(TCNE)_x \cdot y(CH_2Cl_2)$ having $T_C \approx 400$ K[65] and representatives of the $[M(porphyrin)]^{+\bullet}[TCNE]^{-\bullet}$ family.[66]

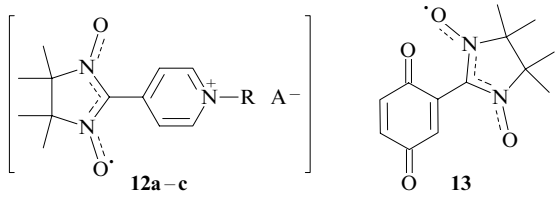
Ferromagnets devoid of metal atoms have also been obtained. Among these, the highest Curie temperature was found for tetrakis(dimethylamino)ethylene complex with fullerene C_{60} (**10**) ($T_C = 16.1$ K).[67] Attempts at more complex pre-organization of spin systems are known,[68] making use of charge transfer complexes incorporating acceptors coupled with spin-labelled donors, for example, such as **11**.[69] In most cases, these complexes behaved as paramagnetic species, except for the ferromagnets ($0.4 \leqslant T_C \leqslant 0.6$ K) described by Sugimoto *et al.*,[70] which are based on charge transfer salts of hexacyanobutadiene (HCBD) or perfluorotetracyanoquinodimethane (TCNQF) with spin-labelled pyridinium salts **12a–c**. Attention is also attracted by ferromagnetic spin interaction in 1,4-dioxocyclohexa-2,5-dienyl nitronyl nitroxide **13**.[71]



10



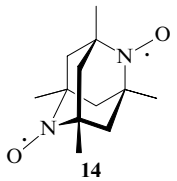
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12a–c **13**

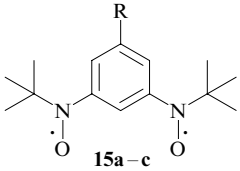
a: R = Me, A = TCNQF;
b: R = Me, A = HCBD;
c: R = Pr, A = TCNQF.

The above methods for the construction of spin clusters, which imply operating with monoradical molecules, do not still allow one to control the molecular packing in the crystal in such a way as to achieve a ferromagnetic exchange between the PMC. Meanwhile, for bi- and polyradicals, methods for orthogonal intramolecular alignment of spins as a result of specially designed molecular structure are known. A remarkable example is targeted synthesis of 1,3,5,7-tetramethyl-2,6-diazaadamantane-*N*,*N*′-dioxyl (**14**), where orthogonality of the magnetic orbitals and, hence, the ferromagnetic intramolecular exchange is ensured by the rigid skeleton of the molecule. In one of the polymorphs of **14**, the intermolecular exchange is ferromagnetic, which accounts for the ability of the phase to undergo transition to the ferromagnetic state at $T_C = 1.48$ K. This T_C value still remains the highest for NR.[72]



14

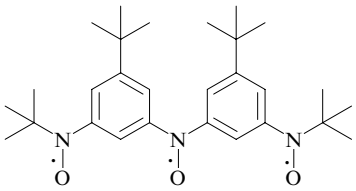
Pre-organization of systems with effective ferromagnetic type exchange can be attained by using nitroxide analogues of alternating non-Kekule systems, their vinylogues or phenylogues. The first such example is biradical **15a** in which two $-N(\dot{-}O)-Bu^t$ fragments are connected by a 1,3-phenylene bridge.[73] For **15a**, $J/k > 300$ K. Biradical **15a** had a low kinetic stability and was converted into 2-amino-4-iminoquinone *N*-oxide. More stable biradicals **15b**,**c** (R = Cl, Br) were retained under ambient conditions, at least, for several weeks.



15a–c

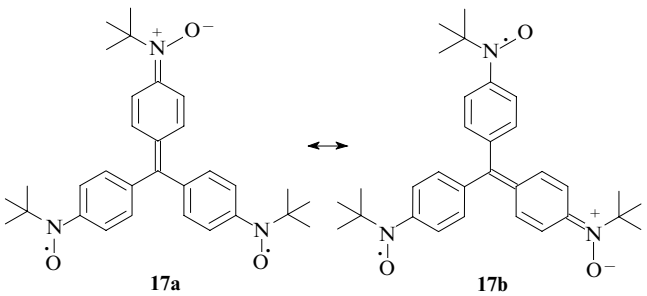
R = H (**a**), Cl (**b**), Br (**c**).

A considerable increase in the stability of phenylene-bound nitroxides was attained by introducing a Bu^t group into the benzene ring. The ground state of the stable triradical **16** is a quartet ($J/k = 240$ K).



16

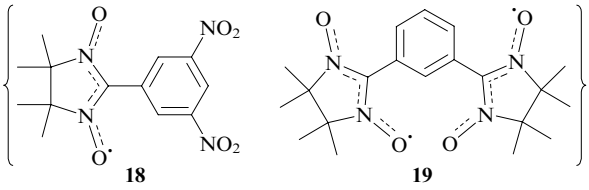
In addition to 1,3-phenylene bridge, the topological model of the simplest biradical, trimethylenemethane, is actively used in the design of high-spin molecules. In particular, it was used in structure planning and in the synthesis of biradical **17**, in the molecule of which strong ferromagnetic exchange takes place ($J/k = 205 \pm 5$ K).[74,75]



17a **17b**

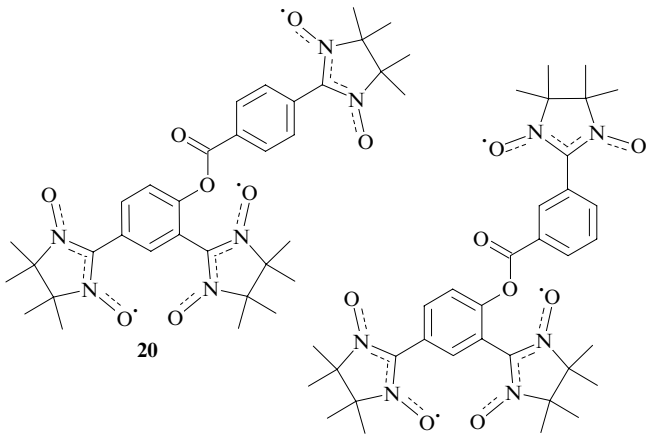
The synthesis of polynitroxides with high-spin ground state opened up the way to targeted assembly of organic ferrimagnets. This assembly was implemented by Japanese researchers,[76,77] who co-crystallized monoradical **18**

($S = {}^1/_2$) and biradical **19** ($S = 1$) and thus prepared a solid phase with stacks of alternating radicals **18** and **19** with ferrimagnetic spin ordering within the stacks at $T < 10$ K according to EPR data.



18 **19**

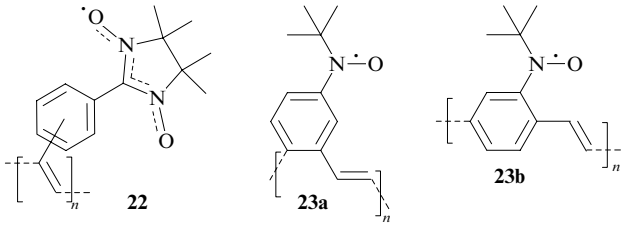
Co-crystallization of different paramagnetic molecules is a rare event. It is more rational to link the high-spin and low-spin components by a particular system of chemical bonds, *i.e.*, actually to fabricate a ferrimagnetic molecular block. According to this idea, a series of polyradicals was obtained. As an example, consider polyradicals **20** and **21** in which the biradical fragment with the triplet ground state is linked by a system of covalent bonds to more remote monoradical fragment.[78, 79] In the biradical fragment, the energy difference between the triplet state and the excited singlet state is $2J/k \approx 20$ K, whereas the interaction energy of the unpaired electrons of this fragment with the unpaired electron of the remote nitronyl nitroxide group is about 0.1 K. Due to this relationship between the intramolecular $2J/k$ values, the biradical and monoradical blocks combined in one molecule behave independently as magnetic subunits. Thus the crystal of **20** is formally composed of chains of alternating bi- and monoradical fragments along which ferrimagnetic ordering of spins $S = 1$ and ${}^1/_2$ takes place at low temperature.



20

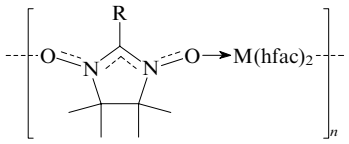
21

Numerous attempts have been made to pre-organize one-dimensional π-bonded systems by polymerization of spin-labelled monomers. During these studies, two general methods for the synthesis of polynitroxides have been developed. The first one can be exemplified by polymerization of ethynylphenyl nitronyl nitroxides in the presence of Rh(COD)(NH_3)Cl (COD is cycloocta-1,5-diene), giving rise to polynitroxides **22** with $M \approx 150\,000$ and spin concentration of ~ 0.95 per monomer unit.[80] It follows from magnetochemical studies that polymers do not tend to undergo ferromagnetic type exchange interactions in the solid state. The second method implies the initial preparation of diamagnetic polyphenylenevinylenes by cross-coupling of *o*- or *p*-bromostyrene monomers bearing the protected hydroxyamino group. The polymers thus obtained were deprotected, oxidized with PbO_2 and used to prepare polymers **23a** and **23b**. The magnetochemical measurements showed that in polymer **23a** with spin concentration of 0.54 in relation to the monomer, ferromagnetic interactions occur between the polymer chains.[81]



22 **23a** **23b**

The polyradical pre-organization with the topological scheme of covalent bonds ensuring the orthogonal arrangement of the magnetic molecular orbitals is a non-trivial task for modern organic chemistry. Even in the case of preparation of high-spin polymers (if only they have not reached the state of single-molecule magnets), the task of their supramolecular organization to ensure a definite system of intermolecular contacts serving as exchange channels (they form conditions for the cooperative magnetic effect) remains hardly practicable. An alternative to this approach to the organization of multispin systems is using heterospin coordination units as the tool for polyradical pre-organization. In this case, targeted self-assembly of the efficiently bound high-dimensional PMC systems is provided due to the ability of the oxygen atom of the $>N\dot{-}O$ group to be coordinated by paramagnetic metal ions. The formation of these systems specifies the primary structure, while its further self-assembly to a three-dimensional crystal structure determining the magnetic properties of the crystalline phase occurs directly during crystallization through weaker non-covalent contacts. This concept was first implemented through the bidentate bridging coordination of nitronyl nitroxides, 2-alkyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl-3-oxides, by Mn^{II} and Ni^{II} hexafluoroacetylacetonates [below referred to as M(hfac)$_2$], which gave rise to heterospin complexes **24**.[82–85] In the crystal structure of the complexes, one can distinguish polymeric chains with strong intrachain antiferromagnetic exchange interactions, which form a differential magnetic moment. In solid phases, a bulk magnetic moment appeared at $T_N \leqslant 8.6$ K due to dipole–dipole interacions between the heterospin chains.



24

R = Me, Et, Pr^i; M = Mn^{II}, Ni^{II}.

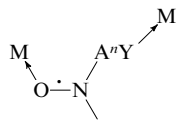
For many nitroxide-containing heterospin complexes studied, a discussion of the magnetic-structure relationships is beyond the scope of this review. We would only note that representative families of compounds that undergo transition to antiferromagnetic, metamagnetic or ferri/ferromagnetic state have been discovered.[8, 68] Among the prepared heterospin complexes, the highest T_C values (46 and 60 K) were found for [{Mn(hfac)$_2$}$_3$**16**$_2$] (Ref. 86) and the Mn(hfac)$_2$ complex with radical **17** (Refs 87, 88), respectively. For heterospin systems based on Cu(hfac)$_2$ com-

plexes with spin-labelled pyrazoles, giant reversible thermostriction was also found and studied in detail.[89–92]

III. Unsaturated nitroxides

The above data demonstrate that nitroxide molecular magnets can in principle be designed in an infinite number of ways. Each research group working in this field brings distinction and ingenuity to the structure of compounds, which are related to their accumulated experience and specific view of the particular task. As a common trend, it can be noted that the development of works along this line is mainly directed to the maximum possible pre-organization of the primary spin systems. A breakthrough in the problem of construction of the solid phase with a desired molecular packing supporting a system of exchange channels was achieved by using complexes of paramagnetic metal ions with nitroxides. Although the problem of deliberate packing of the primary spin systems into a 3D structure favourable for the ferromagnetic type effective exchange interaction still remains unsolved, the achievements are far from being accidental. Every time they came from a highly reasoned synthetic and structural concept of constructing the heterospin system wherein the selection of the paramagnetic ligand is of key importance.

Of the whole diversity of nitroxide types, those able not only to induce the self-assembly of the required polymeric structures but also to function as effective spin density 'conductors' are of particular interest. In addition, a paramagnetic organic compound should be kinetically stable under complexation conditions sufficient for crystallization of the heterospin complex. Preferably, both conditions should be met simultaneously, which can be attained by introducing a specified functional fragment into a nitroxide molecule. Any conjugated π-system with a terminal heteroatom may serve as such fragment efficiently transmitting spin density. Below such systems will be referred to as A^nY, where A^n is a conjugated system without a terminal atom, n is the number of atoms in the A^n system; Y is a terminal donor atom incorporated in the system of conjugation, for example, N or O. The presence of terminal Y atom in the conjugated system with a nitroxide group is of key importance, because it opens up the possibility of bridging coordination of NR to paramagnetic metal ions.



Y = N, O.

Actually the A^nY system specifies a structural template by using which one can distinguish subsets of NR corresponding to a particular structural type among the set of all NR known to date.

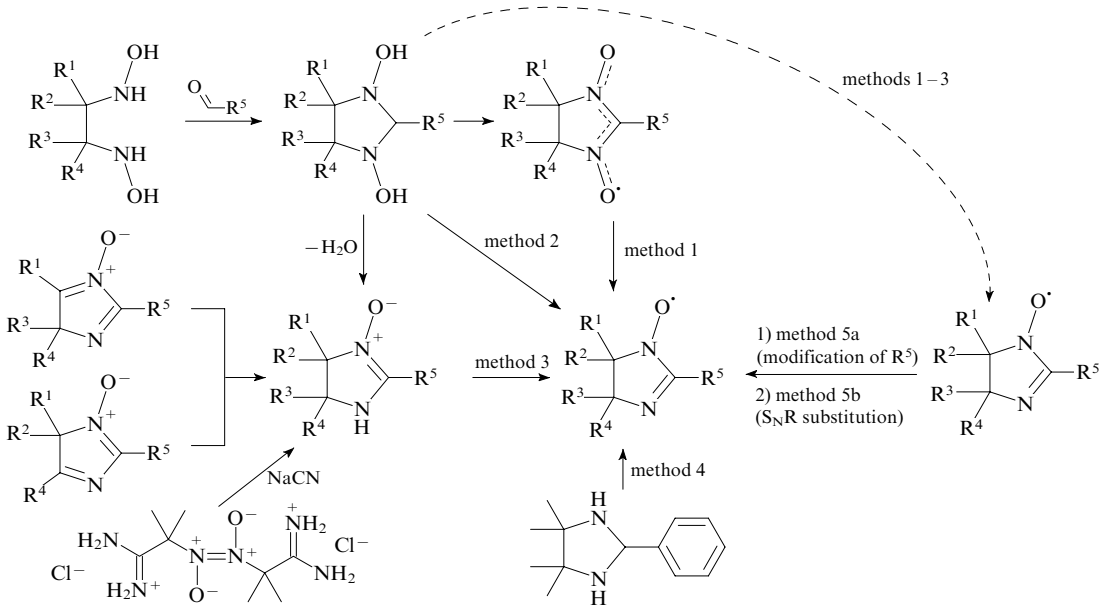
1. The nitroxides O·–N–AY

a. 4,5-Dihydro-1*H*-imidazol-1-oxyls

The series of kinetically inert NR containing an O·–N–AY fragment where AY = –C=N is represented in the Cambridge Crystallographic Data Centre mainly by substituted 4,5-dihydro-1*H*-imidazol-1-oxyls, which are often called 2-imidazolin-1-oxyls or imino nitroxides. Stable 2-imidazolin-1-oxyls are synthesized by a number of methods (Scheme 1).

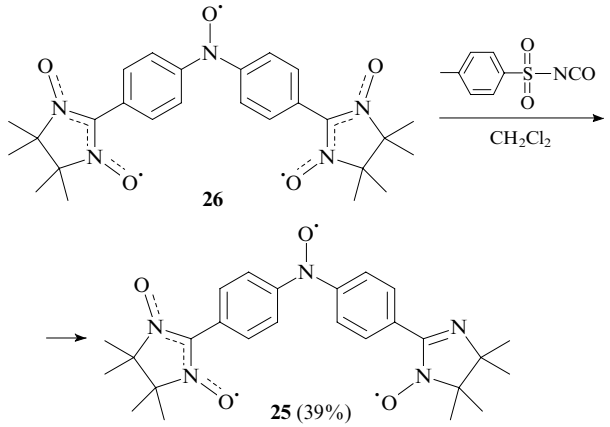
Method 1 implies oxidation of 1,3-dihydroxyimidazolidines to 2-imidazolin-1-oxyl 3-oxides, which are then reduced to 2-imidazolin-1-oxyls, most often, by treatment with nitrous acid generated in the $NaNO_2$–AcOH system (see Scheme 1).[93] This method was used to prepare structurally characterized mononitroxides, for instance, carbamoyl- and cyano-,[94] 3,5-di-*tert*-butyl-4-hydroxyphenyl-,[95] 2-hydroxyphenyl-,[96] pyrazolyl-,[97] *N*-methyltetrazolyl-,[98] pyrenyl-substituted[99] imino nitroxides and 2-imidazoline biradicals.[100] Somewhat modified procedures were also used: for example, 2-methylthio imino nitroxide was prepared using the $NaNO_2$–DMF system,[101] and for the synthesis of imino nitroxide with $R^1 = R^2 = R^3 = R^4 = Me$, $R^5 = Ph$ (yield 87%), the $NaNO_2$–HCl–H_2O–dioxane system was used.[102] The $NaNO_2$–AcOH system proved also to be suitable for deoxygenation of nitronyl nitroxide as a part of the Ni^{II} complex with 2-pyridyl-2-imidazolin-1-oxyl 3-oxide.[103] Cases of spontaneous transformation of 2-imidazolin-1-oxyl 3-oxides to imino nitroxides during comp-

Scheme 1

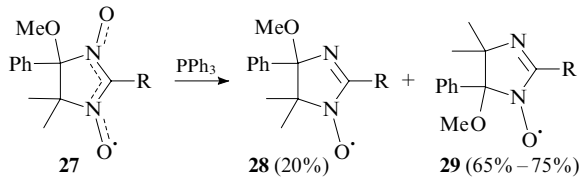


lexation reactions have been reported; hence, it was possible to obtain complexes with labile imino nitroxides. A Cu^{II} bischelate with 2-(2-hydroxy-3-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl, which is unstable in the free state, was obtained in this way.[104]

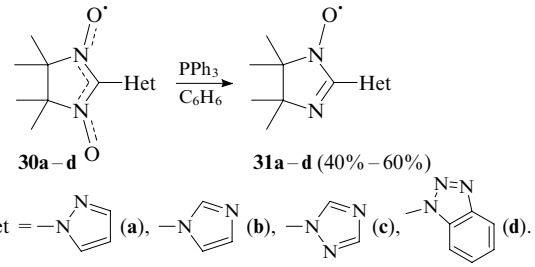
Other reagents for the reduction of 2-imidazolin-1-oxyl 3-oxides to 2-imidazolin-1-oxyls were used much more rarely and, as a rule, in those cases where the $NaNO_2$–acid system was inapplicable. These include highly selective *p*-tolylsulfonyl isocyanate.[93] This can be exemplified by the synthesis of cumbersome polyradical **25** containing three different nitroxide fragments from triradical **26**.[105]



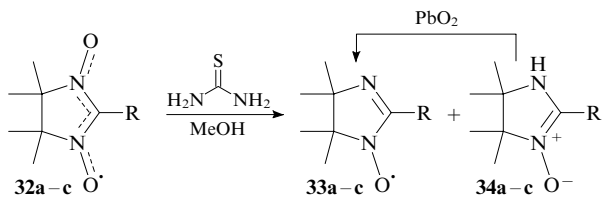
In some cases, PPh_3 is used as the reducing agent;[93] good illustrations are provided by reduction of nitronyl nitroxide **27**, resulting in a mixture of isomeric radicals **28**, **29** (Refs 106, 107) and reduction of readily hydrolyzable compounds **30a**–**d** to radicals **31a**–**d**.[108]



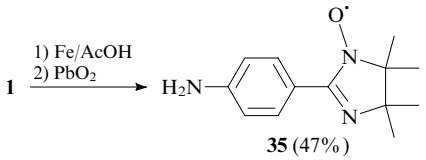
R = Alk, Ar.



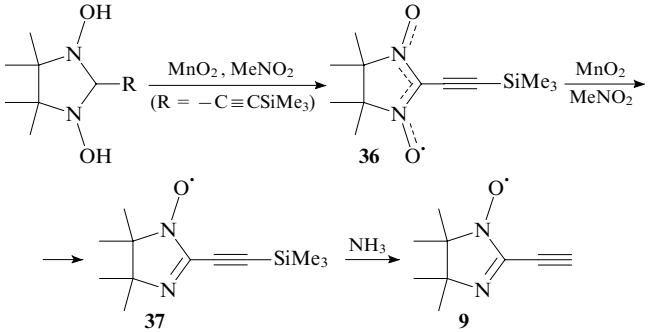
The synthesis of tetrazolyl-substituted imino nitroxide **33c** required selecting special conditions, because nitronyl nitroxide **32c** did not react with PPh_3 and did not give the target product with the $NaNO_2$–AcOH system. Compound **32c** was reduced using the method developed for nitronyl nitroxides **32a**,**b**, specifically, by treating a methanollic solution of nitronyl nitroxide with thiourea followed by the addition of PbO_2. The necessity to add an oxidant is due to the fact that some of radicals **33a**,**b** were further reduced under the reaction conditions to nitrones **34a**,**b**.[109]



In the synthesis of radical **35** with a *p*-aminophenyl substituent, it was also necessary to use PbO_2 in the step of aminonitrone conversion to iminonitroxide.[102]

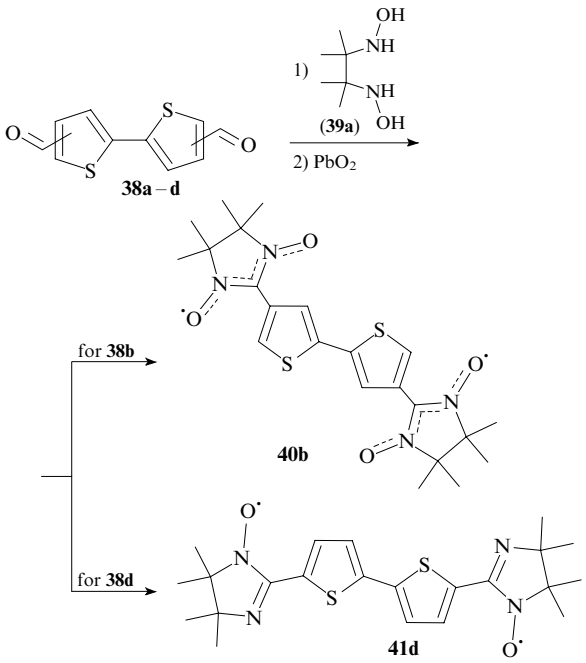


Method 2. A drawback of the synthesis of imino nitroxides by reduction of 2-imidazolin-1-oxyl 3-oxides (method 1) is the formation of amino nitrones, which always accompanies the imino nitroxide synthesis by this method. Method 2, which implies the reaction of 1,3-dihydroxyimidazolidines with MnO_2 in $MeNO_2$, is free from this drawback. Diverse substrates bearing alkyl, aryl or hetaryl groups in position 2 of the heterocycle are converted in high yields to the corresponding imino nitroxides. In essence, this method is a two-step one-pot synthesis. First, 1,3-dihydroxyimidazolidines are oxidized to nitronyl nitroxides, which are then deoxygenated to 2-imidazolin-1-oxyls. Since deoxygenation occurs in the presence of excess oxidant, then unlike method 1, this smoothly gives imino nitroxides in high yields and without amino nitrone impurities. The transformation of 1,3-dihydroxyimidazolidines to imino nitroxides in the MnO_2–$MeNO_2$ system is of particular value for the synthesis of unstable spin-labelled derivatives. Using this approach, nitronyl nitroxide **36** containing a protected acetylene group in position 2 was converted to imino nitroxide **37**, which afforded acetylene derivative **9** on treatment with an alcohol solution of NH_3.[62]

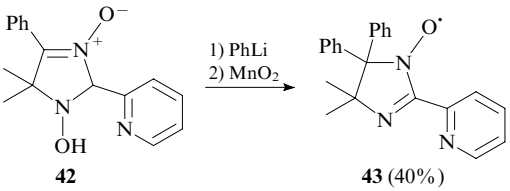


Method 3. A preparative route to imino nitroxides includes oxidation of cyclic amino nitrones (see Scheme 1), for example, 4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole 3-oxides. The latter are produced by thermal dehydration of 1,3-dihydroxyimidazolidines [2-R-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole 3-oxides with R = Me,[110,111] *p*(*m*)-$HO_2CC_6H_4$,[112] precursors of spin-labelled uracil[58] and biradicals with bis(pyrazolyl)pyridine,[113] thiophene-2,4- and thiophene-2,5-diyl[114] bridges were obtained in this way] or by SeO_2-catalyzed[96,115,116] dehydration of 1,3-dihydroxyimidazolidines. Note that the susceptibility of 1,3-dihydroxyimidazolidines for dehydration depends

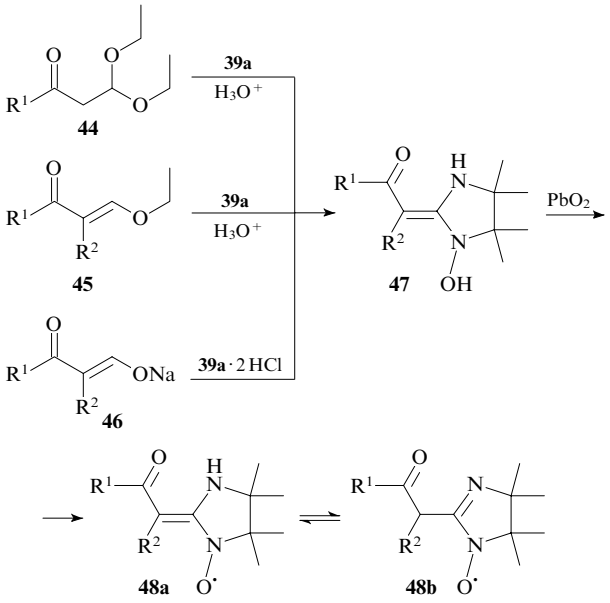
considerably on the nature of substituent R. Thus refluxing 3,3′- (**38a**) or 4,4′-diformyl-substituted (**38b**) 2,2′-bithienyls with 2 equivalents of 2,3-bis(hydroxyamino)-2,3-dimethylbutane (**39a**) in benzene for 20 h followed by PbO_2 oxidation of the reaction product afforded nitronyl nitroxide biradicals **40** (*e.g.*, **40b**) as the major products; under the same conditions, isomeric 4,5′- (**38c**) or 5,5′-diformyl-2,2′-bithienyl (**38d**) yielded only imino nitroxide biradicals **41** (for example, **41d**).[114] Note that methods for the synthesis[117–119] and structure[120] of 2,3-bis(hydroxyamino)-2,3-dimethylbutane (**39a**) were the subjects of special studies.



In some cases, dehydration took place even during preparation of 1,3-dihydroxyimidazolidines under usual conditions, as a result, the latter were formed as mixtures with corresponding nitrones; this can be exemplified by syntheses of 3-thienyl- and 4-(3-thienyl)phenyl-substituted imino nitroxides.[121] Some 2-hetaryl-substituted 1,3-dihydroxyimidazolidines are completely dehydrated even under mild conditions to give aminonitrones; this takes place in the reaction of 1,2,3-triazolecarbaldehyde[122] with **39a** in MeOH. The reaction of 3-imidazoline 3-oxide **42** with PhLi is also accompanied by dehydration to give NR **43** following oxidation.[123]

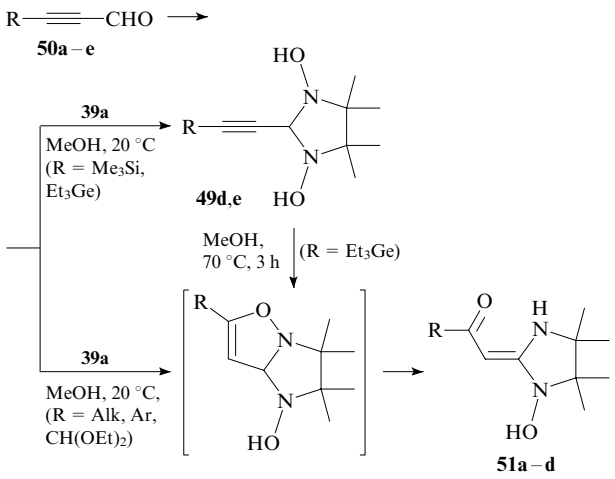


The dehydration that spontaneously takes place in the reaction of synthetic equivalents of 1,3-ketoaldehydes, namely, 1,3-ketoacetals **44** and β-alkoxyvinylcarbonyl compounds **45**, with 2,3-bis(hydroxyamino)-2,3-dimethylbutane (**39a**) in acid medium or in the reaction with the sodium salts of 2-hydroxyvinyl ketones **46** with hydrochloride **39a** results in hydroxyaminoenones **47**, which are precursors of NR **48** existing as either ketovinyl nitroxide (**48a**, type $O\dot{-}N-A^3Y$) or imino nitroxide (**48b**, type $O\dot{-}N-AY$) tautomer.[124] Nitroxides **48a** and **48b** were kinetically unstable.



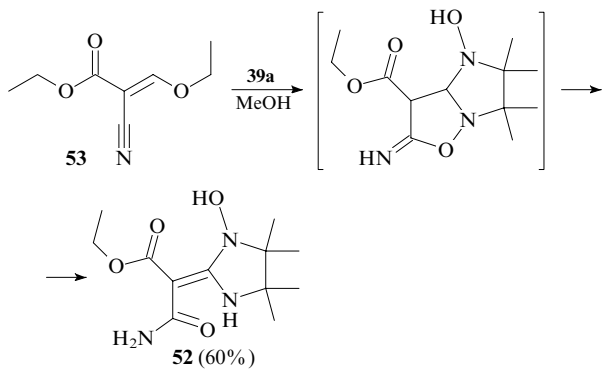
44: R^1 = Me; **45**: R^1 = CF_3, R^2 = H;
46: R^1 = Ph: R^2 = H, Me.

The hydroxyl group in 1,3-dihydroxyimidazolidines **49a–d** can add to the unsaturated fragment in the 2-substituent; this can formally be considered as intramolecular dehydration. The reaction of aldehydes **50a–e** with derivative **39a** gives initially R–C≡C-substituted imidazolidine-1,3-diols. When R = Alk, Ar, the diols are rapidly izomerized to compounds **51a–c**. The rearrangement of derivative **49d** (R = Et_3Ge) to **51d** occurs at a noticeable rate only on heating in MeOH. In the case of compound **49e** (R = Me_3Si), intramolecular addition of the OH group to the C≡C bond could not be performed up to conditions under which dihydroxyimidazolidine started to decompose.[125]

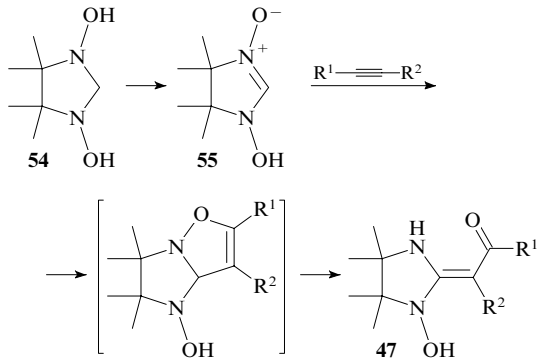


R = Alk (**a**), Ar (**b**), $CH(OEt)_2$ (**c**), Et_3Ge (**d**), Me_3Si (**e**).

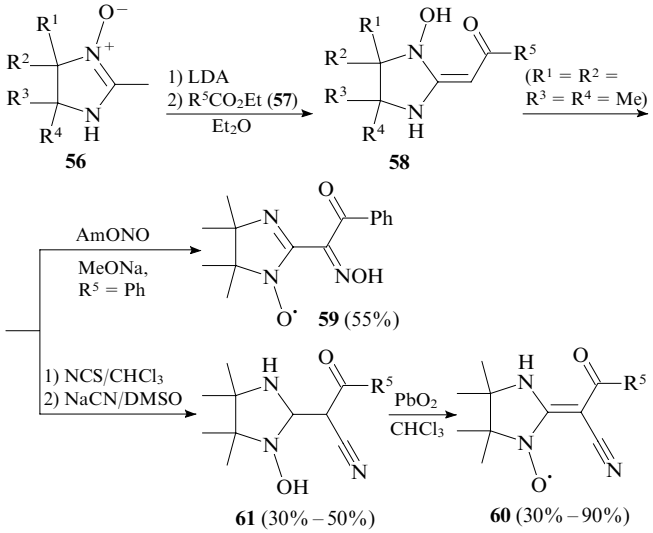
The intramolecular addition of the OH group to the carbon atom of the nitrile group can account for the formation of amide **52** from nitrile **53**.[124]



Formally, dehydration of the 1,3-dihydroxyimidazolidine fragment in 2-unsubstituted derivative **54** can also be accomplished in a two-step process comprising oxidation of **54** to nitrone **55** and the subsequent reaction of nitrone **55** with activated alkynes to give hydroxyaminoenones **47**.



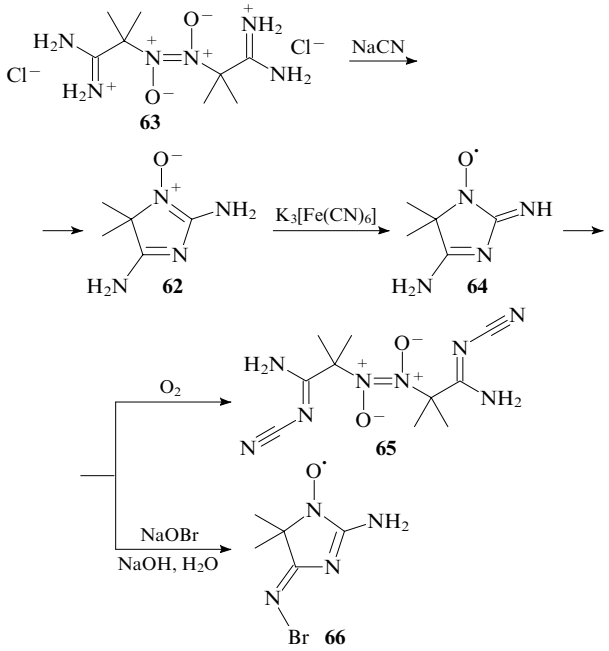
Dehydration of 2-methyl-1,3-dihydroxyimidazolidines followed by modification of the 2-methyl substituent in the resulting cyclic aminonitrones **56** forms yet another synthetic route to various NR. For example, the developed condensation of 2,5,5-trimethyl-4,4-diphenyl-2-imidazoline 3-oxide **56** ($R^1 = R^2 = Ph$; $R^3 = R^4 = Me$) with ethyl benzoate **57** ($R^5 = Ph$) (Ref. 126) was later successfully used to



58: $R^1 = R^2 = R^3 = R^4 = Me$; R^5 = Ph (60%), Me (40%), CF_3 (80%), CO_2Et (40%), 2-Py (55%), 4-Py (35%), Bu^t (60%);
LDA is lithium diisopropylamide, NCS is *N*-chlorosuccinimide.

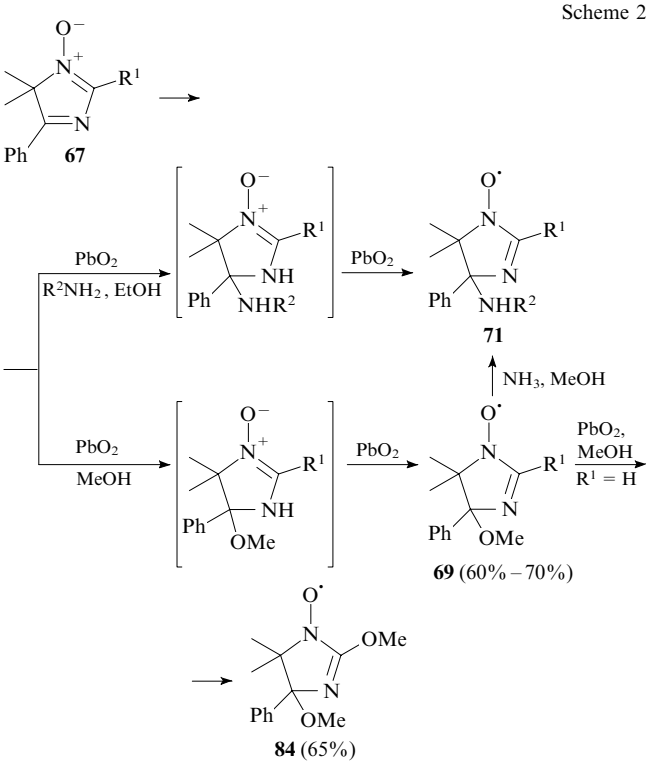
prepare a large group of hydroxyaminoenones **58**, which are precursors of stable nitroxide radicals **59** and **60**.[110, 124] The Ni^{2+}, Co^{2+}, Cu^{2+} and Pd^{2+} ions form stable coordination compounds with some of deprotonated vinyl-substituted NR **60**.

The use of 4*H*-imidazole 1- or 3-oxides markedly extends the scope of method 3, because it opens up the way to 2-imidazolin-1-oxyls with functional groups in positions 4 and 5 of the heterocycle. Thus 2,5-diamino-4,4-dimethyl-4*H*-imidazole 3-oxide (**62**), which is assembled upon the reaction of nitrosoamidine **63** with NaCN, is oxidized to give the Piloty–Scwerin radical **64**, also referring to the O·–N–C=N systems.[127] An aqueous solution of **64** is unstable in air as the compound is readily oxidized to acyclic derivative **65**. The reaction of radical **64** with NaOBr starts with halogenation of the 4-amino(imino) group to give (*Z*)-2-amino-4-bromoimino-5,5-dimethyl-2-imidazolin-1-oxyl (**66**).[128]



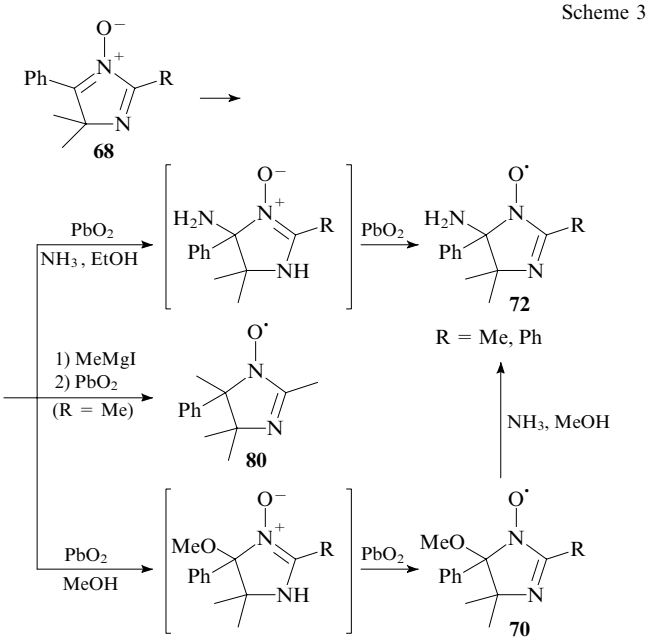
On stirring with PbO_2 in MeOH, 4*H*-imidazole-3- (**67**) and -1-oxides (**68**) furnish 4- (**69**) and 5-methoxy-2-imidazolin-1-oxyls (**70**), respectively. (Note that the reaction of 4*H*-imidazole oxides **67** and **68** with nucleophiles with subsequent oxidation affords not only 2-imidazolin-1-oxyls but also substituted 3-imidazolin-1-oxyls, which are not shown in the schemes.[129]) It cannot be ruled out that during the first step of the one-pot process, a part of PbO_2 is gradually reduced to $Pb(OH)_2$, which is able to deprotonate MeOH and thus promote the nucleophilic addition of the alcohol molecule to the systems of conjugation of oxides **67** or **68** (for details, see the original publication [122]) to give the corresponding nitrones, which are oxidized in the second step under the action of PbO_2 to imino nitroxides. When this reaction is carried out in an ethanol solution of NH_3 or primary amine, a similar process comprising nucleophilic addition of R^2NH_2 and the subsequent oxidation of aminonitrone may take place; consequently, 4*H*-imidazole *N*-oxides **67** and **68** are converted to 4- and 5-amino-2-imidazolin-1-oxyls **71** and **72**, respectively (Schemes 2 and 3).

Scheme 2



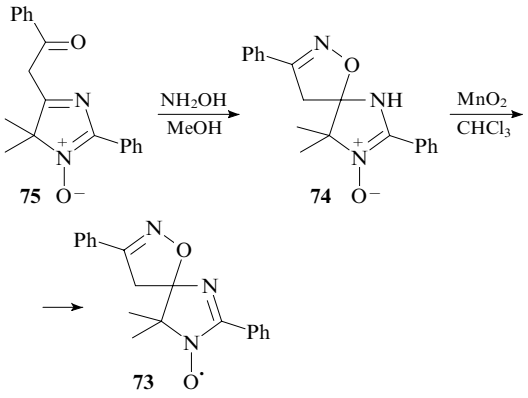
R^1 = H, Me, Ph; R^2 = H, Me.

Scheme 3

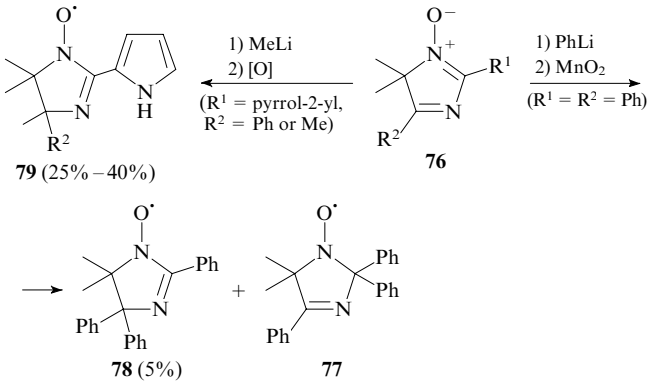


70: R = Me (70%), Ph (90%), *m*-$O_2NC_6H_4$ (90%), *p*-$Me_2NC_6H_4$ (30%).

The paramagnetic spiro compound **73** is formed in ~50% yield in the oxidation of cyclic amino nitrone **74** obtained by reaction of 4*H*-imidazole 3-oxide **75** with NH_2OH in methanol.[126]



2-Imidazolin-1-oxyls can be synthesized by the addition of organolithium compounds to 4*H*-imidazole 3-oxides **76**. When planning this synthesis, one should take into account the known data on the reaction regioselectivity. Thus compound **76** (R^1 = R^2 = Ph) reacts with PhLi mainly at the nitrone fragment to give 3-imidazolin-1-oxyl **77**; the yield of 2-imidazolin-1-oxyl **78** does not exceed 5%. The reaction of **76** (R^1 = pyrrol-2-yl; R^2 = Me or Ph) with MeLi involves exclusively the imine fragment, thus ensuring the formation of polyfunctional imino nitroxides **79**.[123]

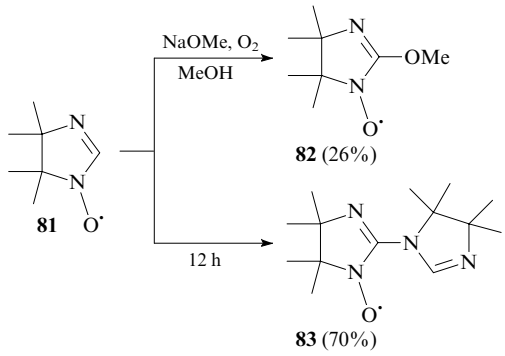


A similar strategy was also used to introduce an alkyl substituent into 4*H*-imidazole 1-oxide **68** (R = Me). For this purpose, compound **68** was made to react with MeMgI, and then the addition product was oxidized to NR **80** (see Scheme 3),[10] or PhLi was added to oxide **68** (R = Ph or 2-Py), and then cyclic hydroxyamine was oxidized with MnO_2 to the NR.[123]

Method 4 for preparing imino nitroxides directly from imidazolidines was implemented for only one example of 4,4,5,5-tetramethyl-2-phenylimidazolidine oxidation with H_2O_2 in the presence of Na_2WO_4 ($MeOH-H_2O$, 20 °C, 12 h; yield 41%).[119]

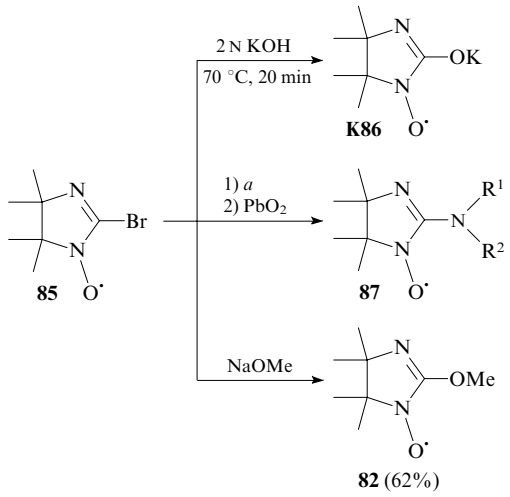
Methods 5a and 5b are based on substitution reactions and modification of substituents located in different positions of 2-imidazolin-1-oxyls. Pay attention to H atom replacement by a functional group, *i.e.*, to the processes that should formally be classified as S_NH reactions. Thus heating of nitroxide radical **81** in MeOH in the presence of

NaOMe and atmospheric oxygen gives radical **82**. Another example of S_NH reaction is spontaneous transformation of solid **81** predominantly to product **83** on overnight storage.



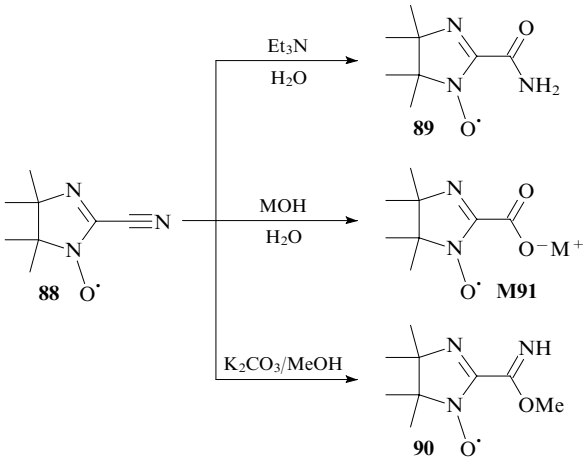
One more example of substitution of the OMe group for an H atom is transformation of NR **69** to dimethoxy derivative **84** (see Scheme 2).

Groups located at any carbon atom of the heterocycle can be substituted. Thus 4- or 5-methoxy-2-imidazolin-1-oxyls **69** and **70** are converted to amino derivatives **71** and **72** when kept in a water–alcohol solution of NH_3 for 60 h (see Schemes 2 and 3). The bromine atom in 2-bromo-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl (**85**) is readily substituted on treatment with nucleophiles: stirring of a suspension of **85** in 2 N KOH at 70 °C affords a solution of paramagnetic anion **86**; the reaction of bromo derivative of **85** with NaOMe in methanol at ~25 °C is completed after 1 h by the formation of NR **82**. Under conditions of bromine replacement by the HNR^1R^2 amino group to give radical **87** (60–100 °C, 1.5–5 h), the nitroxide group is converted to the >N−OH group, and for its oxidation, PbO_2 is added to the reaction mixture at the final stage.[101]



$R^1 = R^2 = H$: (*a*) NH_3 (conc.), ~100 °C, 5 h, 70%;
$R^1 = H$, $R^2 = Pr^i$: (*a*) H_2NPr^i, H_2O, 55–60 °C, 4 h, 44%;
$R^1 = R^2 = Me$: (*a*) 50% $HNMe_2$, refluxing for 90 min, 52%.

Among examples of the synthesis of 2-imidazolin-1-oxyls based on modification of substituents, those that ensure the preparation of NR inaccessible by other methods deserve attention. Thus the C≡N triple bond in radical **88** is fairly reactive, which was used to convert this compound to amide **89** under mild conditions (H_2O/Et_3N, 6 h, 20 °C) (55%)[94] and to imidate **90** (MeOH, K_2CO_3, 2 h, yield 36%).



M = Li^+ (**Li91**), K^+ (**K91**), Bu_4N^+ (**Bu_4N91**).

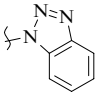
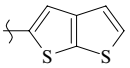
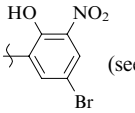
Hydrolysis of NR **88** in the presence of an equimolar amount of MOH ($M^+ = Li^+$, K^+, NBu_4^+) gives radical salts **M91** in 86%–97% yields. The structure of the solid phase of such salts was studied by X-ray diffraction using the potassium salt **K91**.[130] Anion **91** is able to substitute the acetate ion in $M(OAc)_2$ salts, which was used for the synthesis of a series of heterospin complexes $Cu(\mathbf{91})_2(MeOH)_2$, $Cu(\mathbf{91})_2(H_2O)_2$, $Cu(\mathbf{91})_2$, $Co(\mathbf{91})_2(MeOH)_2$, $Ni(\mathbf{91})_2(H_2O)_2$, $Ni(\mathbf{91})_2(Py)_2$ and $Ni(\mathbf{91})_2(4,4'\text{-bipyridyl})(H_2O)$ with greater ferromagnetic type intramolecular exchange interactions. For complexes $Cu(\mathbf{91})_2$ and $Ni(\mathbf{91})_2(4,4'\text{-bipyridyl})$, cooperative magnetic ordering effects were recorded at 16.6 and 4.6 K, respectively.

Properties and correlations. According to Cambridge Crystallographic Data Centre,[131] which contains data on 53 2-imidazolin-1-oxyls, statistically the most probable bond lengths O−N, N(1)−C(2) and C(2)=N(3) are in the ranges of 1.26–1.28, 1.35–1.42 and 1.27–1.30 Å, respectively. Table 1 presents the geometric parameters of some 2-R-4,4,5,5-tetramethyl-2-imidazolin-1-oxyls. The imidazoline ring in 2-imidazolin-1-oxyls is non-planar; the C(4)−C(5) bond is rotated with respect to the ONCN fragment by an angle of 10 to 18°. The dihedral angle α does not exceed, most often, several degrees; this ensures effective overlap of the frontier orbitals of the π-systems of the substituent and the paramagnetic fragment. The solid phases of known 2-imidazolin-1-oxyls are characterized by weak temperature dependence of the effective magnetic moment [$\mu_{eff}(T)$]. *N*-Azolyl-substituted imino nitroxides characterized by rather strong antiferromagnetic type exchange interactions are exceptions (see Table 1).

b. 1,4,5,6-Tetrahydropyrimidin-1-oxyls

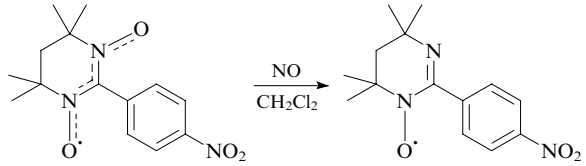
Nitroxide **92a**, which is the only representative of 1,4,5,6-tetrahydropyrimidin-1-oxyls studied by X-ray diffraction analysis, was prepared by bubbling NO through a solution of nitronyl nitroxide **93a** in CH_2Cl_2. In radical **92a**, the O−N, N(1)−C(2) and C(2)=N(3) bond lengths are 1.278, 1.416 and 1.275 Å, respectively. The spin density distribution in imino nitroxide **92a** reflects the values of a_N 0.982 and 0.401 mT (H_2O), which differ from those for

Table 1. Geometric parameters, packing details and exchange parameters for some 2-R-4,4,5,5-tetramethyl-2-imidazolin-1-oxyls.

R	d_{N-O} /Å	$d_{C(2)-N(1)}$ /Å	$d_{C(2)=N(3)}$ /Å	α /deg [a]	β /deg [b]	Packing details, exchange parameters /K	Ref.
	1.265	1.368	1.257	36.7	17.7	dimers; $2J/k = -95.8$ [c]	108
	1.276	1.383	1.264	22.0	15.7	dimers; $2J/k = -51.7$ [c]	108
	1.267	1.318	see [d]		0.0	layers; $2J/k = -24.0$ [e]	94
	1.272	1.403	1.282	1.6	10.7	dimers; $2J/k = -9.2$ [c]	132
 (see [f])	1.268 1.273	1.402(8) 1.401(8)	1.276(7) 1.252(9)	4.7 6.5	13.4 14.6	dimers; $2J/k = -3.2$	96
	1.266	1.391	1.287		15.0	chains ≡C−H···N; weak AF interactions	62
	1.292	1.393	1.275	3.2	10.8	layers; weak AF interactions	130

[a] Dihedral angle between the plane of the ONCN fragment and plane of the substituent R. [b] Angle between the straight line through the C(4)−C(5) atoms in the imidazoline ring and the ONCN plane. [c] Dimer model. [d] Disorder of the O atom over two positions with 0.5 weight. [e] Cyclic trimer model. [f] Two independent molecules.

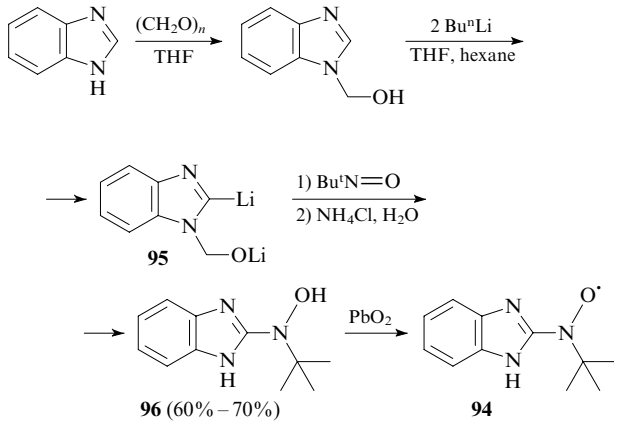
4,4,5,5-tetramethyl-2-(4-nitrophenyl)-4,5-dihydro-1*H*-imidazol-1-oxyl (0.90 and 0.435 mT) determined under the same conditions.[133]



93a **92a** (93%)

c. 2-Hetaryl-*tert*-butyl nitroxides

2-Hetaryl-*tert*-butyl nitroxides refer to the class of stable paramagnetic compounds that satisfy the condition O÷N−A^{1}N. Below, using the synthesis of 2-(*N*-*tert*-butyl-*N*-oxylamino)benzoimidazole (**94**) as an example, it is demonstrated that a typical method for the preparation of this class of compound includes the reaction of organolithium compound **95** with 2-methyl-2-nitrosopropane followed by oxidation of the *N*,*N*-disubstituted hydroxylamine **96** on treatment with PbO_2 or Ag_2O.[134]



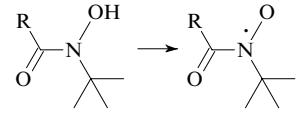
95 **96** (60%−70%) **94**

The known 2-hetaryl-*tert*-butyl nitroxides are red-coloured compounds, their kinetic stability increases with extension of the π-system in the hetaryl substituent; therefore, they can be isolated in a free state (Table 2).

The coordination of these NR by metal ions can also serve as additional stabilizing factor. Thus 2-pyridyl-*tert*-butyl nitroxide (**97**) reacts with Ni^{II} or Cu^{II} perchlorates to give stable bis-chelate complexes $[Ni(\mathbf{97})_2(H_2O)_2](ClO_4)_2$ (Fig. 2) and $[Cu(\mathbf{97})_2(ClO_4)_2]$ characterized by strong intramolecular ferro- (J/k = 126 K for Ni complex) or antiferromagnetic ($J/k = -137$ K for Cu complex) exchange interaction between the unpaired electrons.[139]

d. Carbonyl nitroxides

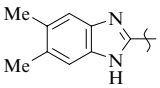
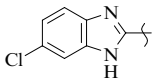
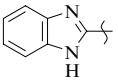
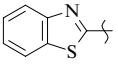
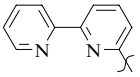
Considering the data of the Cambridge Crystallographic Data Centre, it can be concluded that some acyclic acyl nitroxides and amidoyl nitroxides are stable in the absence of hydrogen atoms at the α-carbon atom of the nitroxide group and can be isolated in a pure state. Thus single-electron oxidation of *N*-*tert*-butyl-substituted hydroxamic acids **98a**,**b** yields the corresponding *N*-*tert*-butyl-3,5-dinitrobenzoyl (**99a**) and *N*-benzoyl-*N*-*tert*-butyl nitroxides (**99b**), their dark green colour is due to long-wavelength absorption band with a maximum at about 645 nm. *N*-*tert*-Butyldialkylaminocarbonyl nitroxides, for example NR **99c**, were prepared in a similar way.[140]



98a−**c** **99a**−**c**

R = 3,5-$(O_2N)_2C_6H_3$ (**a**), Ph (**b**),  (**c**).

Table 2. Yield in the oxidation step, geometric parameters, HFC constants, packing details and exchange parameters for 2-hetaryl-*tert*-butyl nitroxides.

Hetaryl substituent	Yield (%)	HFC constant /mT	Bond lengths (d/Å) and dihedral angles (α/deg)	Packing details, exchange parameters	Ref.
	10	a_{NO} 1.025, $a_{C=N}$ 0.218, a_{NH} 0.039, a_H 0.019–0.131 [a]	d_{N-O} = 1.280 $d_{N-(BIm)}$ = 1.389 $\alpha_{ONCN(H)}$ = −3.4	dimers; $2J/k$ = −48.0 K	135
	37	a_{NO} 1.0, $a_{C=N}$ 0.212, a_{NH} 0.044, a_H 0.045–0.085 [a]	d_{N-O} = 1.278 $d_{N-(BIm)}$ = 1.386 $\alpha_{ONCN(H)}$ = −9.2	dimers; $2J/k$ = −44 K	136
	92	a_{NO} 1.016, $a_{C=N}$ 0.213, a_{NH} 0.079, a_H 0.022–0.086 [a]	d_{N-O} = 1.283 $d_{N-(BIm)}$ = 1.392 $\alpha_{ONCN(H)}$ = −8.7	layers; $2J/k$ = −3 K	134
	85	a_{NO} 0.916, $a_{C=N}$ 0.267, a_H 0.033–0.131 [b]	oil [c]	–	137
	85	a_{NO} 1.050 [d]	oil [e]	–	138

BIm is benzoimidazole. [a] In benzene. [b] In CH_2Cl_2. [c] UV/vis (MeOH) λ_{max} (ε) = 482 (3180), 512 (3540), 557 nm (3090). [d] In toluene. [e] UV/vis ($CHCl_3$) λ_{max} (ε) = 474 (702), 513 nm (450).

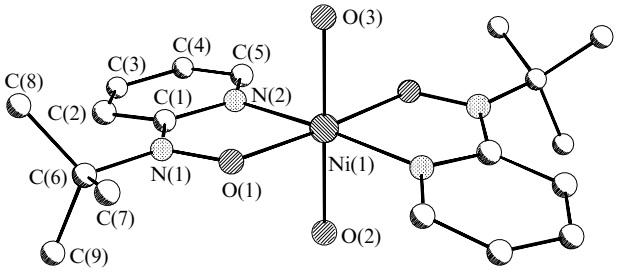
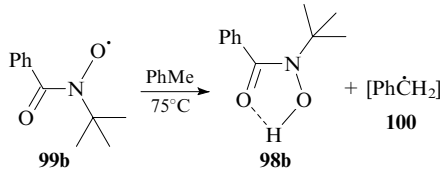
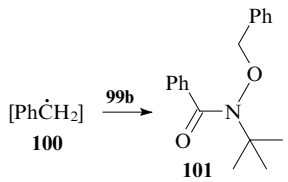


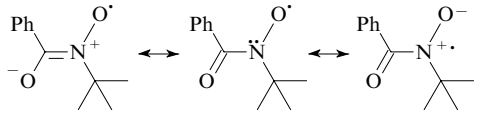
Figure 2. Structure of bis-chelate in the complex $[Ni(\mathbf{97})_2(H_2O)_2].(ClO_4)_2$.

The presence of the carbonyl group conjugated with a nitroxide fragment in acyl- and amidoyl nitroxides imparts clear-cut oxidizing properties to these compounds.[141] For example, unlike $Bu^t-N(\dot{-}O)-Bu^t$, *N*-benzoyl-*N*-*tert*-butyl nitroxide (**99b**) reacts with the solvent on heating in toluene at 75 °C ($\tau_{1/2} \approx 30$ min) giving rise to hydroxamic acid **98b** and its benzyl ester **101** by a pathway involving generation of the benzoyl radical **100**. The formation of a strong intramolecular H-bond in the reduction product, hydroxamic acid, is one of the factors facilitating the reaction.



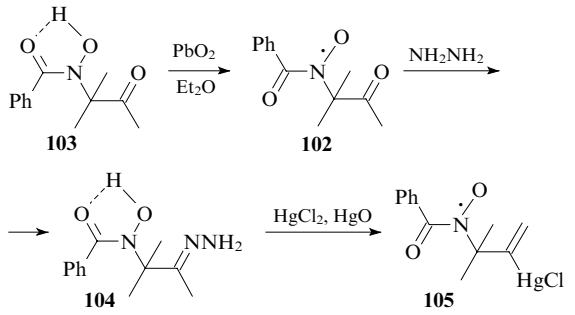


In addition, high reactivity of acyl nitroxides is related to the considerable degree of localization of the unpaired electron on the O atom of the $>N\dot{-}O$ group due to its effective conjugation with the carbonyl group, as indicated by the much smaller a_N constants of **99a**–**c** (~0.8 and 1.17 mT for **99a**,**b** and **99c**, respectively) compared with the di-*tert*-butyl nitroxide (~1.55 mT).



The π-conjugation of carbonyl and nitroxide groups in carbonyl nitroxides **99a**–**c** did not affect the $N\dot{-}O$ bond length, which is typical of NR [1.275(6) Å].[131] The C=O bond lengths in NR **99a** and **99c** are equal to within the experimental error [1.206(6) Å], whereas the C(=O)–N bond lengths, equal to 1.384(7) and 1.452(4) Å, respectively, are considerably different. This is due to not only the competing conjugation of the carbonyl group with the piperidine N atom in **99c** but also to much smaller dihedral angle O–N–C–O in solid **99a** (116.9°) compared to that in solid **99c** (166.3°).

The high susceptibility of carbonyl nitroxides for the reduction seems to preclude the expectation of their successful participation in chemical reactions not involving the nitroxide group. The possibility of modification of the functional group in carbonyl nitroxides by reactions giving final products in which the radical centre can be easily regenerated has yet been scarcely studied. Only one mention of the successful use of this approach for acyl nitroxide preparation can be found in the literature. The first step of the process includes the proper preparation of stable acyl nitroxide **102** by oxidation of ketohydroxamic acid **103** with lead dioxide. The reaction of compound **102** with NH_2NH_2 affords diamagnetic hydrazone **104**, which is converted to an organomercury radical **105** on treatment with $HgCl_2$ and HgO in ether.[10]



2. Nitroxides O·–N–A²Y

a. 4,5-Dihydro-1*H*-imidazol-1-oxyl 3-oxides

4,5-Dihydro-1*H*-imidazol-1-oxyl 3-oxides, which are often referred to in the literature as 2-imidazolin-1-oxyl 3-oxides, α-nitronyl nitroxides or nitronyl nitroxides, have proved long ago to be valuable paramagnetic organic blocks for the design of molecul magnets. This accounts for the considerable progress in the development of the chemistry of these compounds and their key precursors (Scheme 4).

Method 1. The most widely used method 1 comprises reaction of vicinal bis(hydroxyamine) with aldehyde or its synthetic equivalent followed by oxidation of the 1,3-dihydroxyimidazolidine thus formed.[142,143] The use of this method requires the search for preparative methods for the synthesis of key vicinal bis(hydroxyamines). Methods for the preparation of 2,3-bis(hydroxyamino)-2,3-dimethylbutane (**39a**) and racemic mixtures of 2,3-bis(hydroxyamino)-2-R-3-methylbutanes (**39**) [R = C_8H_{17}, $MeOCH_2$, $THPOCH_2$ (THP is tetrahydropyranyl), $AcOCH_2$ and so on] can be found in the literature.[118,119,144]

The conditions of aldehyde condensation with vicinal bis(hydroxyamine) **39a** vary depending on the nature of the carbonyl compound (Table 3). The reaction is carried out in water if aldehydes or acetals are sufficiently water soluble. Compound **39a**·H_2SO_4·H_2O is added to an aqueous solution or suspension of aldehyde, and after completion of the condensation, the solution is neutralized with $NaHCO_3$, and the precipitated adduct is filtered off (Table 3, entries *1* and *2*). Good results are obtained when the condensation of soluble aldehydes with 2,3-bis(hydroxyamino)-2,3-dimethylbutane (**39a**) is carried out in methanol; 1,3-dihydroxyimidazolidines thus formed are often separated to the solid phase as analytically pure compounds (Table 3, entries *3* and *4*). When the **39a**·H_2SO_4–K_2CO_3–MeOH system was used, the yields of the adducts are usually substantially lower (entry *5*). The condensation of low reactive aldehydes with **39a** requires specific conditions (entry *6*). Azulene-1-carbaldehyde, azulene-1,3-dicarbaldehyde and DMF do not react with **39a**.

In the case of low solubility of aldehyde in MeOH or EtOH, the rate of its reaction with **39a** sharply decreases. As a consequence, the condensation starts to be complicated by side processes involving compound **39a** and the solvent, and the amount of products formed in these processes becomes comparable or exceeds the amount of the condensation products.[118] In this case, the effective concentration of the aldehyde can be increased by selecting the solvent and increasing the temperature of the reaction mixture (entries *7* and *8*). An alternative approach is to apply conditions under which compound **39a** is stable for a long period of time (many days), for example, stirring of a suspension of the reactants in C_6H_6 under inert atmosphere (entry *9*).

The above-listed examples are also applicable to condensation of 2,3-bis(hydroxyamino)-2,3-dimethylbutane (**39a**) with dialdehydes (entries *10*–*14*) and polyaldehydes. However, it should be borne in mind that during the reaction the substrate solubility sharply decreases after the formation of the monoadduct, which can almost completely remove it from the area of subsequent transformations. Caneschi *et al.*[156] deliberately used this circumstance for the transformation of isophthalic aldehyde to 2-(3-formylphenyl)-substituted nitronyl nitroxide. To introduce all aldehyde groups in the reaction, a compromise synthesis is required, which would ensure the solubility of all intermediate substrates and minimize decomposition of **39a**. For example, in the synthesis of 1,3-alternate calix[4]arenes **106** and **107** functionalized at the upper rim by two and four nitronyl nitroxides, di- and tetraaldehyde was condensed under inert atmosphere with 5 and 10 equivalents of **39a**, respectively, in the presence of 0.2 molar equivalents of

Scheme 4

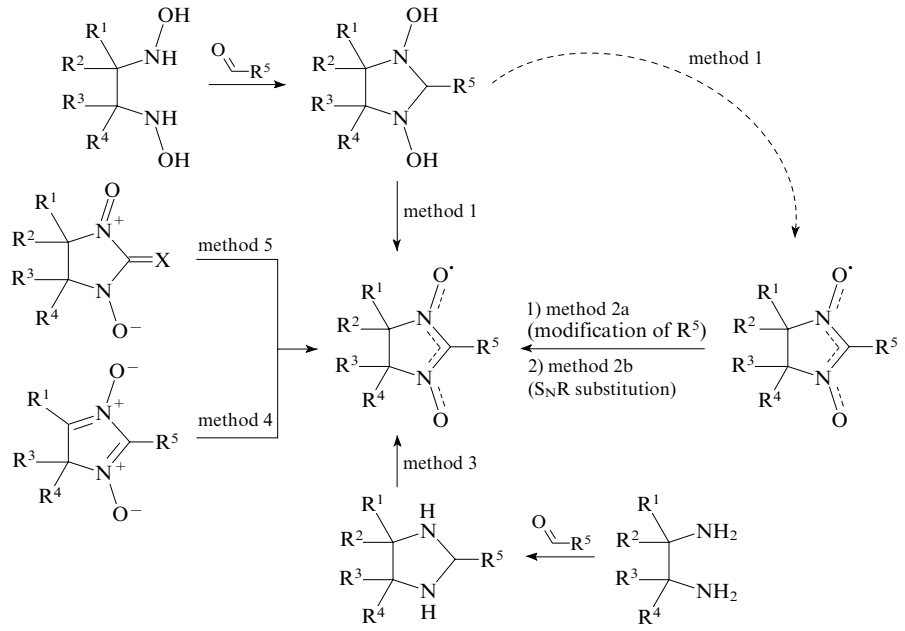
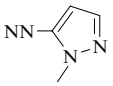
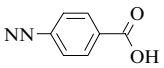
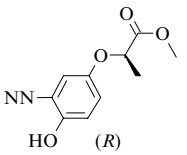
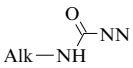
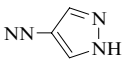
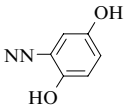
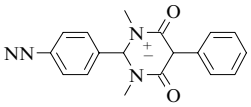
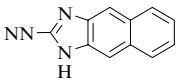
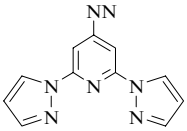
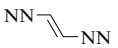
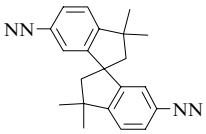
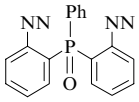
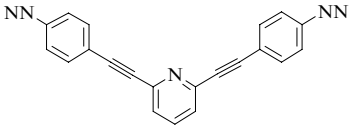
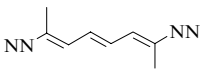
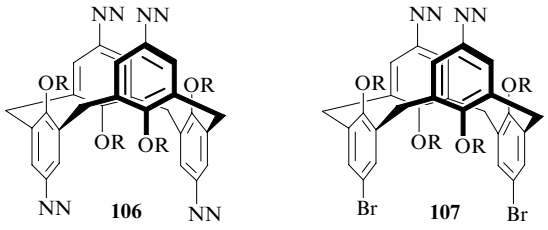


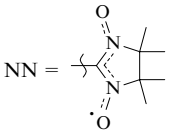
Table 3. Preparation conditions and yields of 2-imidazolin-1-oxyl 3-oxides.

Entry	Structural formula [a]	Condensation conditions; yield	Oxidation conditions; yield	Ref.
1		**39a** · H_2SO_4 · H_2O, Na_2CO_3, H_2O, 50 °C, 2 h; 72%	$NaIO_4$ (2.0 equiv.), $CHCl_3$, H_2O, 0 °C, 50 min; 39%	145
2		**39a** · H_2SO_4 · H_2O, $NaHCO_3$, H_2O, 96 h; 85%	$NaIO_4$ (1.5 equiv.), H_2O, 10 min; 65%	146
3		**39a** (1.2 equiv.), MeOH, 25 °C, ~12 h	$NaIO_4$ (1.0 equiv.), CH_2Cl_2, H_2O, 0 °C, 30 min; overall yield 10%	147
4		**39a** (1.0 equiv.), MeOH, 25 °C, ~12 h	$NaIO_4$ (2.0 equiv.), CH_2Cl_2, H_2O, 0 °C, 10 min; overall yield ~70%	148
5		**39a** · H_2SO_4 · H_2O, MeOH, K_2CO_3, 24 h; 20% (see [b])	$NaIO_4$ (1.5 equiv.), CH_2Cl_2, H_2O, 0 °C → 25 °C, 12 min; 50% – 75%	149
6		**39a** (0.85 equiv.), **39a** · H_2SO_4 · H_2O (0.02 equiv.), pulverized molecular sieves 3 Å, inert atmosphere, 5% MeOH in C_6H_6, 4 days, 88%	PbO_2, pulverized molecular sieves 3 Å, inert atmosphere, THF, 10 min; 88%	41
7		**39a** (1.5 equiv.), MeOH – $CHCl_3$ (1 : 2), 60 °C, 18 h; 52%	PbO_2 (9 equiv.), DMF, 3 days; 54%	150
8		**39a** (1.5 equiv.), *N*-methylpyrrolidone, heating at 130 °C for 10 min and at 25 °C for 48 h	$NaIO_4$ (6 equiv.), CH_2Cl_2, H_2O, 0 °C; 25%	51
9		**39a** (1 equiv.), C_6H_6, 25 °C, 2 weeks; product was not isolated	$NaIO_4$ (1 equiv.), $CHCl_3$, H_2O; 42%	151
10	 (see [c])	**39a** · H_2SO_4 · H_2O, MeOH, H_2O, 20 h	$NaIO_4$ (3.0 equiv.), CH_2Cl_2, H_2O, 1 h	152
11		**39a** (2.0 equiv.), EtOH, 30 °C, 64 h; 77% (crude)	$NaIO_4$ (0.1 equiv.), MeOH, 5 min; 26%	153
12		**39a** (2.0 equiv.), MeOH, inert atmosphere, reflux, 6 h; 60% (crude)	$NaIO_4$ (3.0 equiv.), CH_2Cl_2, H_2O, 20 min	154
13		**39a** (2.5 equiv.), a PhMe – MeOH mixture (2 : 1 by volume), inert atmosphere, reflux, 48 h; 61% (crude)	$NaIO_4$ (2.8 equiv.), $CHCl_3$, H_2O, 10 min; 34%	155
14		**39a** (2.0 equiv.), C_6H_6, azeotropic distillation, 30 min	$NaIO_4$ (3.0 equiv.), CH_2Cl_2, H_2O, 1 h	152

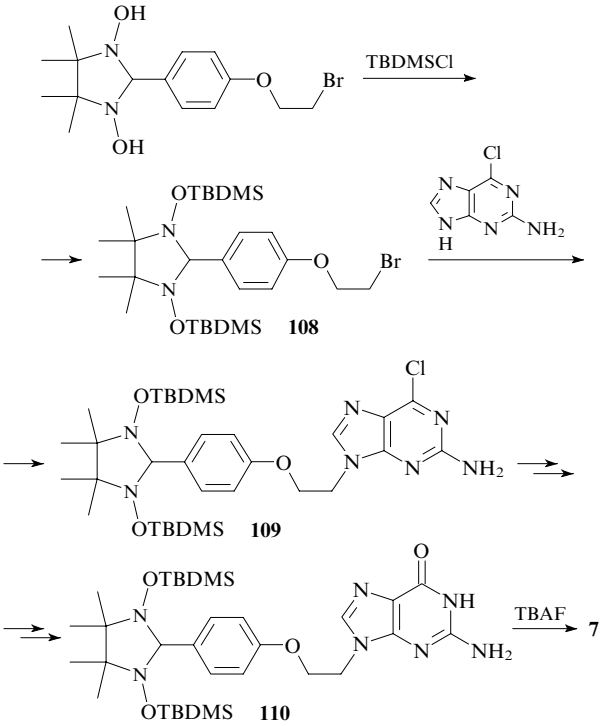
[a] NN is 4,4,5,5-tetramethyl–1-oxyl-3-oxide-imidazolin-2-yl. [b] The reaction carried out under conditions of entry *1* gave the adduct in 68% yield. [c] (*E*)-1,1,4,4-Tetraethoxybut-2-ene served as the starting compound.

TsOH in MeOH at 55–65 °C for 2–3 days.[157] In some cases, it is sufficient to pass a slow flow of gaseous argon above the reaction mixture of polyaldehyde and **39a**.[158]





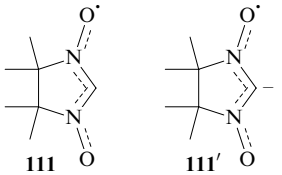
To complete consideration of the specific features of preparation of 1,3-dihydroxyimidazolidines as the starting compounds in the nitronyl nitroxide synthesis by method 1, we would like to note that the OH groups of dihydroxyimidazolidine can be protected, if necessary, by reaction with Bu^tMe_2SiCl (TBDMSCl) in the presence of imidazole (DMF, 50 °C). For example, this strategy makes it possible to replace the halogen atom in derivative **108** by a purine base (K_2CO_3, KI, DMF, 60 °C, 25 h) and to convert then compound **109** to substituted guanine **110**. Deprotection of **110** on treatment with 1.0 M TBAF (TBAF is tetrabutylammonium fluoride) in a THF–DMF mixture (14 h, 25 °C) affords the target nitronyl nitroxide **7**.[60]



In the vast majority of cases, 1,3-dihydroxyimidazolidines were oxidized by $NaIO_4$ in a $CHCl_3–H_2O$ or $CH_2Cl_2–H_2O$ two-phase system (see Table 3). As regards the amount of $NaIO_4$ needed to attain the optimal yields of nitroxides, different opinions exist. Suffice it to say that Ullman *et al.*[142] applied 1.5 moles of $NaIO_4$ to oxidize 1 mol of the monoadduct, and in another publication,[153] it is noted that 0.05 moles of $NaIO_4$ was used for the same purpose; often 0.5 to 1 mole of the oxidant is used. Our opinion is as follows. In oxidation of 1,3-dihydroxyimidazolidines, it is better to minimize the amount of $NaIO_4$. In order to avoid local increase in the oxidant concentration, it should be added to the reaction mixture in portions with vigorous stirring in air over a period of 1–2 h at ~5–10 °C. Under these conditions, 0.8 moles of $NaIO_4$ per mole of 1,3-dihydroxyimidazolidine is most often sufficient. The failure to meet the above conditions may result in product contamination by impurities difficult to separate, which was observed many times in experiments on the synthesis of pyrazolyl-substituted nitronyl nitroxides carried out by one of us.

For oxidation of 1,3-dihydroxyimidazolidines, PbO_2 (see Table 3, entries *6* and *7*) and MnO_2 are used rather often. These reagents have an important feature, namely, when the reaction is carried out in widely used MeOH and EtOH, the hydroxides $Pb(OH)_2$ and MnO(OH) formed in the active form can induce solvent ionization. As shown below, this may initiate subsequent transformations of nitronyl nitroxide such as formation of coordination compounds, nucleophilic addition of a solvent molecule to the unsaturated fragment and so on.

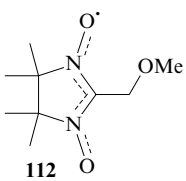
Method 2 [C(2)-functionalization]. 2-Imidazolin-1-oxyl 3-oxides can undergo reactions in which the O·–N–A^2O fragment remains intact, which considerably extends the range of accessible polyfunctional paramagntic molecules of this type. A representative group of such transformations is C(2)-functionalization of 2-unsubstituted nitronyl nitroxide **111,** which is promoted by high CH-acidity of the nitronyl nitroxide fragment.



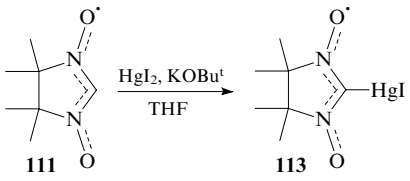
Indeed, whereas at pD < 7, the rate constant for the exchange of H(2) by a D atom in D_2O does not depend on the OD^- concentration ($k_{296\,K} \approx 3.3 \times 10^{-3}\ s^{-1}$), in the range of 7 < pD < 8, the constant $k_{296\,K}$ increases linearly with increase in $[OD^-]$ according to the relation $k_{296\,K} \approx 3.6 \times 10^4 [OD^-]\ s^{-1}$, and at pD > 8 it becomes too high and beyond the scope of experimental possibilities. By equating the rates of the forward (v^+) and back (v^-) reactions for

111 + OD^- ⇌ D_2O + **111′**,

taking place in the range of 7 < pD < 8 and assuming that v^- is determined by the rate of diffusion, 5×10^{10} litre $(mol\ s)^{-1}$, one can calculate the pK_a(**111**) value, which is 21.9. This is in full agreement with EPR data according to which nitroxide **111** (a_N = 0.726 mT, a_H = 0.344 mT) reacts with $KOBu^t$ in DMSO to be fully converted to organopotassium compound **K111′** (a_N = 0.849 mT). On treatment with $ClCH_2OMe$, this product yields methoxymethyl-substituted derivative **112** in 24% yield.

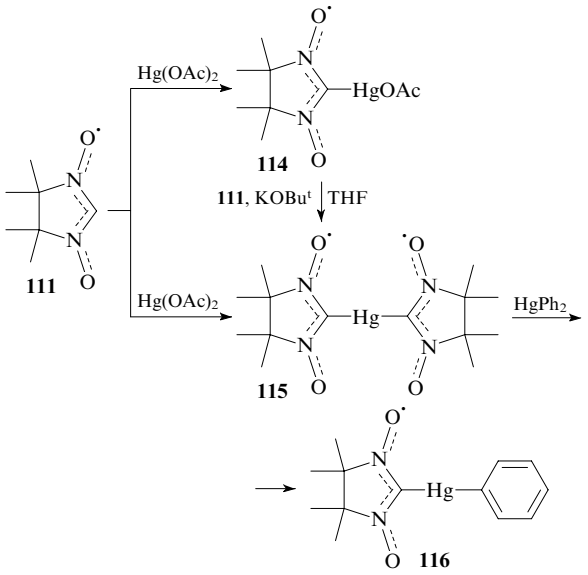


The low yield of product **112**, caused by decomposition of **K111′** in DMSO (at room temperature complete decomposition is attained in 30 min),[159] prompted studies aimed at the search for efficient C(2)-functionalization of nitronyl nitroxide **111**. The decisive step along this line was made by Leute and Ullman,[160] who patented the preparation of a large series of organomercury nitroxides. An example is compound **113**, which was prepared by stirring nitronyl nitroxide **111** with excess HgI_2 and $KOBu^t$ in THF.



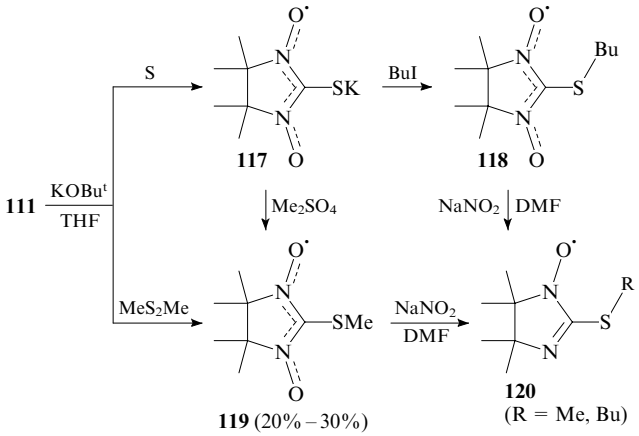
This reaction, as indicated in the patent, is of general value and can also take place with other mercury salts, for example, $HgCl_2$, HgF_2, $Hg(NO_3)_2$, $Hg(CN)_2$ and $HgSO_4$. Monosubstituted mercury carboxylates **RCO_2Hg111'** are formed on direct reaction of **111** with an equivalent amount of $Hg(O_2CR)_2$. For example, NR **114** was obtained in 62% yield by heating **111** with $Hg(OAc)_2$ in CH_2Cl_2 in the presence of AcOH and Ac_2O for 10 min; the researchers noted that the reaction was rather insensitive to the solvent nature. This conclusion was later confirmed by German chemists who carried out this reaction in MeCN for 24 h and obtained compound **114** in 77% yield.[161]

One more merit of Leute and Ullman[160] is the fact that they discovered the ability of NR **114** to readily exchange the acetate anion on treatment with a variety of reagents. The mercury-bound AcO^- ion can be replaced by the OH^-, Hal^-, NO_3^-, N_3^-, ClO_4^-, ArO^- and other anions. Thus NR **114** reacts with LiCl in THF for 15 min to give **ClHg111′** in 72% yield. In addition, NR **114** undergoes AcO^- exchange by other groups when reacts with amines, alcohols and carbanions. An interesting example is the synthesis of bis(4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-2-yl-1-oxyl 3-oxide)mercury (**115**) (yield ~65%) from nitronyl nitroxides **114** and **111** in the presence of $KOBu^t$ (THF, 25 °C, inert atmosphere, 1 h). More recently the method for preparation of biradical **115** was markedly simplified: it was reduced to stirring of **111** with $Hg(OAc)_2$ in H_2O or MeOH. The product yield (60%) was not affected by the presence of Et_3N in the solution.[162]

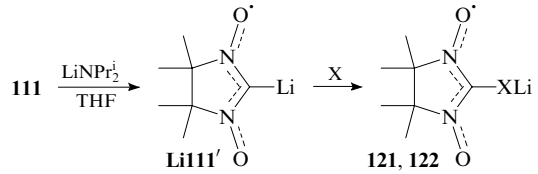


The chemical behaviour of biradical **115** is typical of organomercury compounds, for example, it undergoes exchange by organic residues with other mercury compounds. Thus refluxing of **115** with $HgPh_2$ in CH_2Cl_2 for 1 h gave radical **116** in ~70% yield. Biradical **115** easily forms complexes with chelating ligands, namely, *o*-phenanthroline, TMEDA, 2,2′-bipyridyl,[160] and is coordinated by $Cu(hfac)_2$ to give various polynucluear complexes: $[\mathbf{115}]_2[Cu(hfac)_2]_4$ and $[\mathbf{115}]_2[Cu(hfac)_2]_4 \cdot 2\,C_6H_6$.[162]

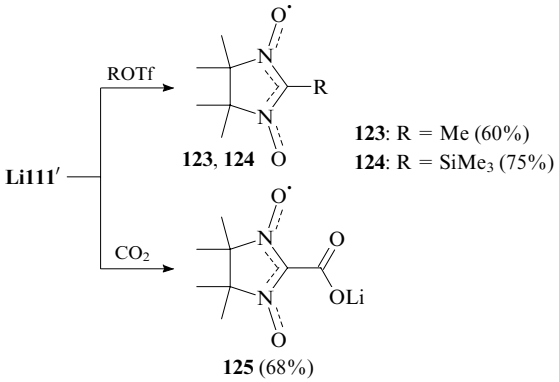
The $KOBu^t-THF$ system was also used in the synthesis of a series of mercapto-substituted 2-imidazolin-1-oxyls **117**–**120**.[101]

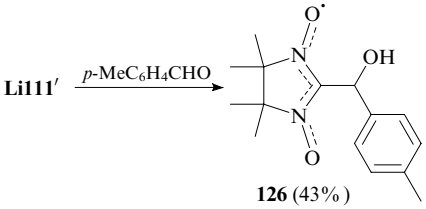


Weiss *et al.*[161] described some C(2)-functionalization reactions that imply preliminary preparation of **Li111′** in THF at −78 °C by treatment of **111** with $LiNPr^i_2$. This is accompanied by the change in a solution colour from violet to red. It is noteworthy that replacement of $LiNPr^i_2$ by LiBu is impossible under these conditions as this causes destruction of **111** giving unidentified diamagnetic products. The subsequent addition of electrophiles to a solution of **Li111′** gave NR **121**–**126** containing SLi, SeLi, Me, $SiMe_3$, CO_2Li or $CH(OH)C_6H_4Me$-4 substituents.[161]

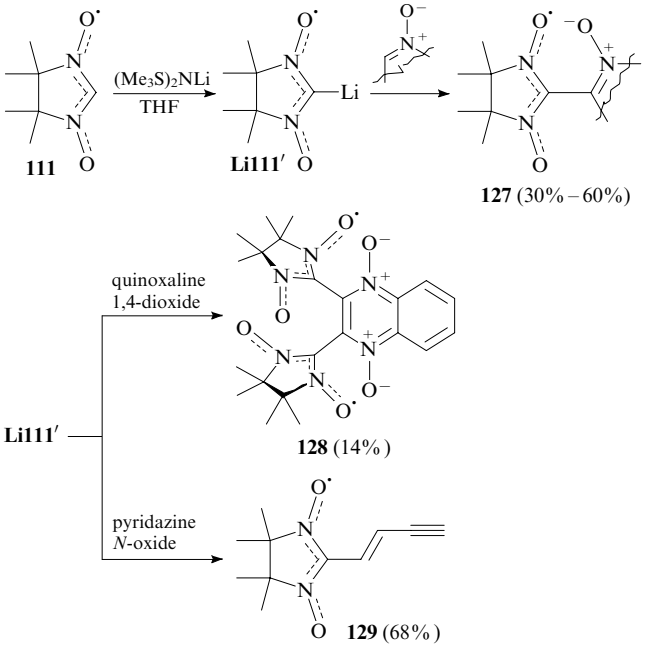


X = S (**121**, 80%), Se (**122**, 55%).

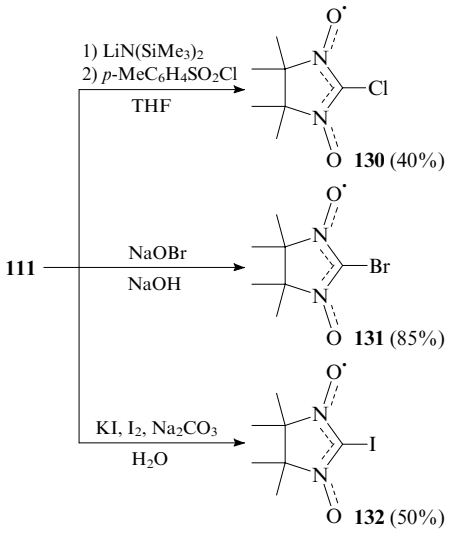




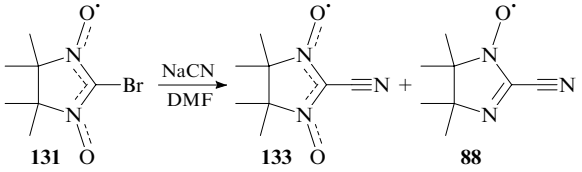
Using radical **Li111′**, convergent routes for the synthesis of polyfunctional nitronyl nitroxides were implemented. Using S_NH strategy,[163, 164] a general method for the preparation of hetaryl-substituted nitronyl nitroxides based on the reaction of **Li111′** with azine *N*-oxides was developed.[165] A solution of $(Me_3Si)_2NLi$ in THF was added with stirring at a temperature of about −90 °C to a solution of **111** in dry THF and after 0.5 h, a solution of azine *N*-oxide in THF was added. The S_NH reactions of pyridine, pyrimidine, pyrazine, isoquinoline, phthalazine, quinoxaline and 1,2,4-triazine *N*-oxides with **Li111′** afforded the corresponding nitronyl nitroxides **127**. Quinoxaline 1,4-dioxide furnished biradical **128**, and pyridazine *N*-oxide formed the enyne-substituted nitronyl nitroxide **129**.[166]



A number of methods of halogenation of nitronyl nitroxide **111** are known. For preparation of chlorinated derivative **130**, a solution of *p*-$MeC_6H_4SO_2Cl$ was added at −80 °C to a solution of **Li111′** in THF. The reaction mixture was kept until it warmed-up to room temperature, then diluted twofold with n-heptane, and filtered. Several drops of Et_3N were added to the filtrate and the mixture was concentrated at a reduced pressure to give crude **130**. Brominated derivative **131** is prepared most often by a modification of the procedure proposed by Boocock and Ullman:[167] a cold solution of **111** in CH_2Cl_2 is shaken in a separating funnel with an alkaline solution of NaOBr for 30–40 s at ~0 °C,[168] the organic layer is separated, several drops of Et_3N is added, and the mixture is filtered through Al_2O_3. The filtrate is diluted with heptane and concentrated at 20–25 °C until crystals of the product start to precipitate; for completion of the crystallization, the flask is kept at −10 °C for 14 h. Crystallization of both **130** and **131** is performed in a CH_2Cl_2–heptane mixture but as in the isolation, several drops of Et_3N are necessarily added to the solution to prevent decomposition of halogenated derivatives to zwitter-ions. The iodinated derivative **132** is prepared in a ~50% yield by the reaction of **111** with KI and I_2 in the presence of Na_2CO_3 or with ICN in water in the presence of $NaHCO_3$.[167]

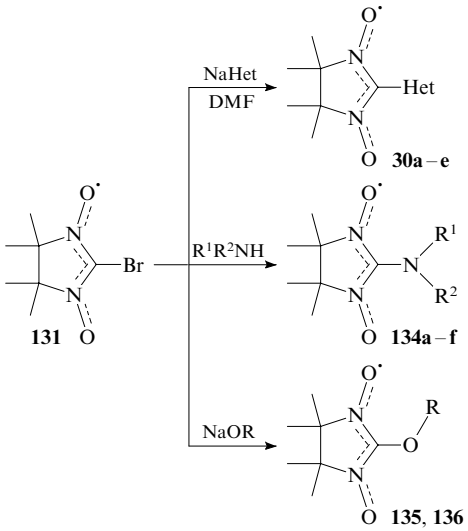


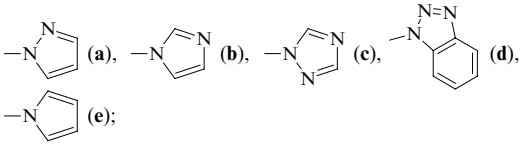
Method 2 (substitution). The halogen atoms in halo derivatives **130** and **131** can be substituted by nucleophiles. When using this reaction for the preparative synthesis of nitronyl nitroxides, the experimental details should be thoroughly obeyed. This is due to insufficient stability of both the starting halo derivatives and the final nitronyl nitroxides. For example, in the synthesis of nitrile **133**,[169–171] in order to maximize the reaction yield, the bromo derivative **131** is made to react with NaCN in DMF at 55–60 °C (the temperature inside the vessel) in the presence of Et_3N. The process is arrested when the concentration of **133** has reached a maximum (~40 min) to isolate nitrile **133** (60%) and the product of its deoxygenation **88** (15%).[94] Note that a temperature rise by 10–15 °C results in complete transformation of nitronyl nitroxide **133** to imino nitroxide **88** over a period of 15 min.[93]



Every reaction of bromo derivative **131** with particular N-nucleophile requires optimization of the reaction conditions, which may considerably differ. Thus the formation of the amino-substituted derivative **134a** was detected upon bubbling NH_3 for 2 h through a heated (65–70 °C) solution of **131** in concentrated aqueous ammonia. The reaction of **131** with Me_2NH in water is more vigorous ending in the formation of **134b** during the same period of time but at ~25 °C (performing the reaction at ~0 °C for 4 h affords **134b** in 55% yield). The reaction of **131** with aziridine is carried out in the presence of Et_3N in boiling anhydrous ether for 3 h to give compound **134e** in 13% yield, whereas the replacement of bromine by a morpholine residue took place on stirring of a mixture of **131** with morpholine for 1 h at 0 °C and then for 12 h at ~25 °C to isolate **134f** in 46% yield.[101, 168] For the synthesis of *N*-azolyl-substituted nitronyl nitroxides **30a–d**, bromo derivative **131** is treated

with the sodium salt of a heterocyclic compound (pyrrole, pyrazole, imidazole, 1,2,4-triazole, benzotriazole); the process is carried out in DMF at 40–45 °C for 6 h.[108, 172] The corresponding alkoxy derivatives **135** and **136** are prepared by the reaction of **131** with NaOEt in EtOH and with NaOBn in $MeOCH_2CH_2OMe$ (20 min, ~25 °C).[167]

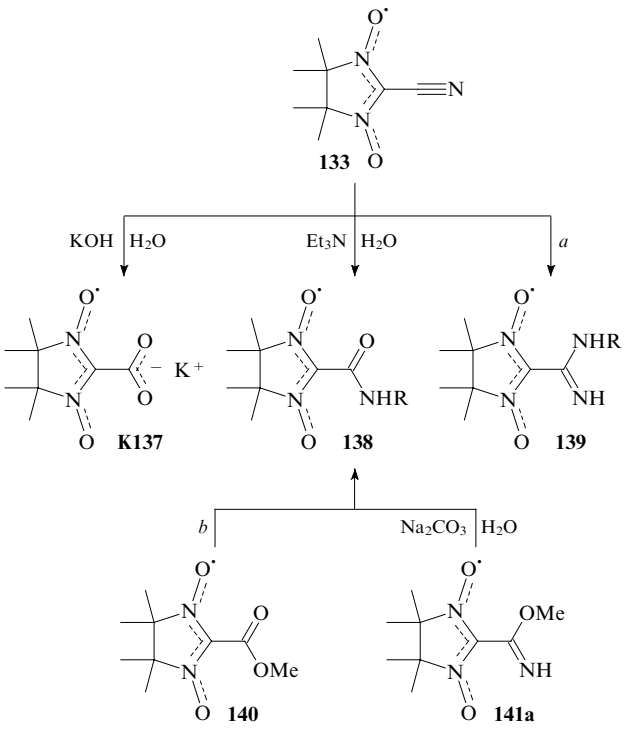


30: Het =  (**a**), (**b**), (**c**), (**d**), (**e**);

134: R^1R^2N = NH_2 (**a**), Me_2N (**b**), Et_2N (**c**), Pr^iNH (**d**), aziridine (**e**), morpholine (**f**);
135: R = Et; **136**: R = Bn.

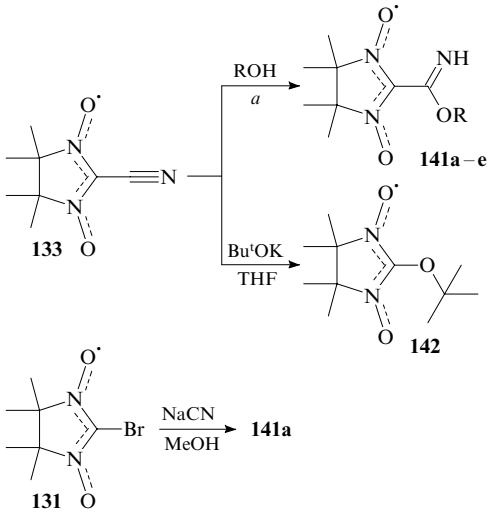
Method 2 (**substituent modification**). Among this type of reactions, of most interest is the possibility of preparing 2-substituted 2-imidazolin-1-oxyl 3-oxides that cannot be synthesized by method 1. Considering these reactions is reasonable to start with the addition to multiple bonds of nucleophiles and dipoles that change the surrounding of the α-carbon atom of the substituent. This can be exemplified by diverse transformations of derivatives of carboxylic acid, 2-carboxy-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide. Thus paramagnetic salt **K137**, amides **138** and amidines **139** are prepared from nitrile **133**, ester **140** or imidate **141a** as shown below.[94, 169, 173] Carboxylate **137** is stable in the solid state as a salt, while in solution it is spontaneously decarboxylated to give nitronyl nitroxide **111**.[146]

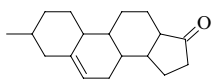
Imidates **141a–e** are readily formed upon the alcohol addition to the triple bond of nitrile **133**. Imidates **141a**,**b** (R = Me, Et) are formed on stirring **133** in an appropriate alcohol in the presence of Na_2CO_3. For the synthesis of imidates[169] **141c**,**d** (R = Pr^i, Bu^n), THF was introduced additionally to the reaction mixture because nitrile **133** is insoluble in Pr^iOH and BuOH.[174] The addition of heavy alcohols, for example, 3-β-hydroxy-17-ketoandrost-5-ene, to the triple bond of **133** is carried out in pyridine in the presence of NaH. Methyl imidate **141a** can be prepared directly from bromide **131** if its reaction with NaCN is carried out in MeOH (60 °C, 30 min, yield 45%).[169] It is



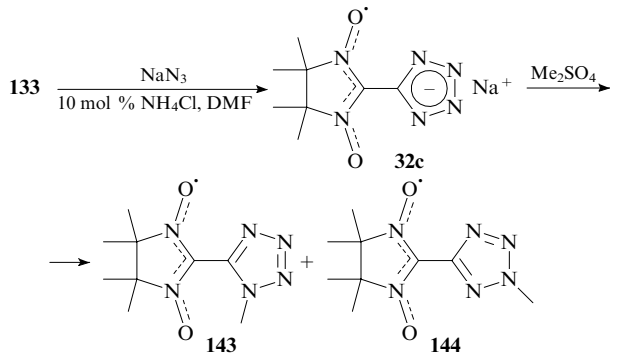
(*a*) $NH_2CH_2CH(OEt)_2$, PhMe, 80–90 °C, 30 min or $BnNH_2$, MeCN, 15 min; (*b*) NH_3, H_2O, ~100 °C, 3 min or $BnNH_2$, MeCN, 15 min.

noteworthy that nitrile **133** in the THF–Na_2CO_3 system does not react with Bu^tOH but when $KOBu^t$ is used, the nitrile group is replaced by a Bu^tO group.[174]



141: R = Me (**a**), Et (**b**): (*a*) Na_2CO_3;
R = Pr (**c**), Bu^n (**d**): (*a*) Na_2CO_3, THF;
R =  (**e**): (*a*) NaH, Py.

The reaction of nitrile **133** with NaN_3 in DMF in the presence of 10 mol% NH_4Cl at 60 °C results in spin-labelled sodium tetrazolate **32c** (77%).[175] Then, by reducing the temperature of the reaction mixture to 50 °C, the product can be methylated by Me_2SO_4 and both isomers, **143** (66%) and **144** (20%), can be isolated.[98]



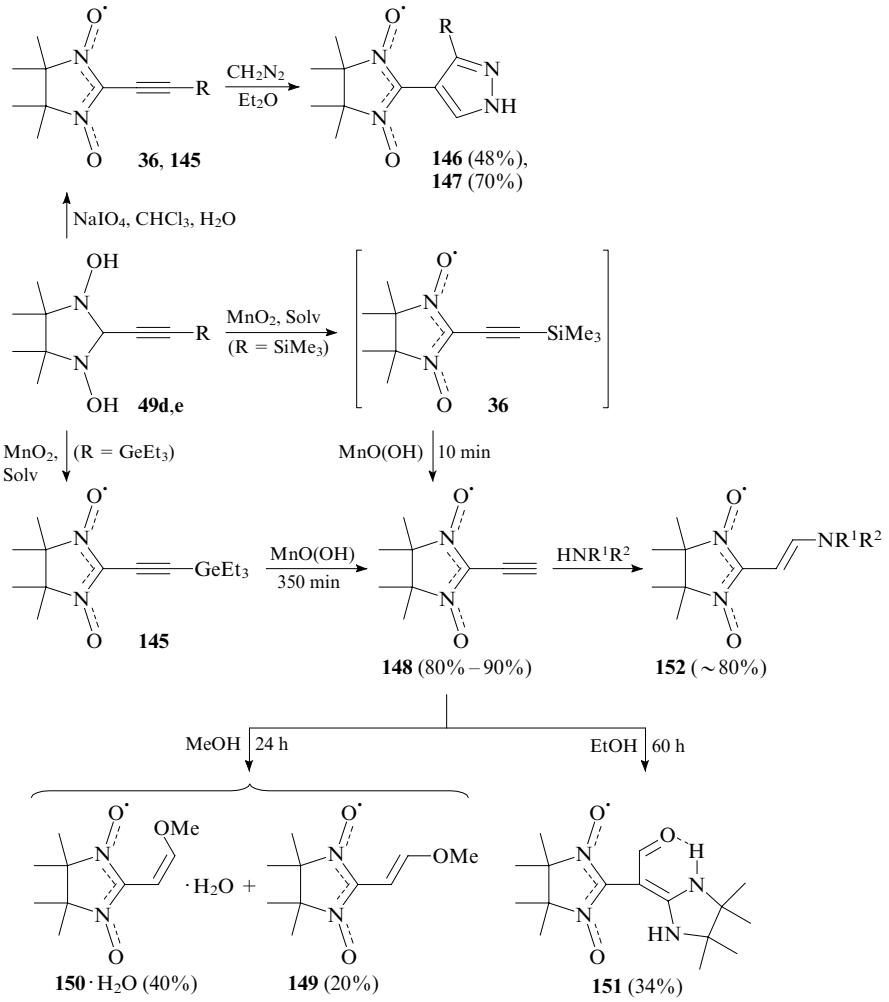
The $Et_3Ge-C\equiv C-$ and $Me_3Si-C\equiv C-$ substituents in position 2 of dihydroxyimidazolidine hamper the intramolecular addition of the OH group to the triple bond, which allows one to use compounds **49d**,**e** in the synthesis of acetylene derivatives of 2-imidazolin-1-oxyl 3-oxides **36** and **145** (Scheme 5). The latter slowly add CH_2N_2 (this is especially true for silyl-substituted acetylene **36**); the reaction is regioselective and gives the corresponding spin-labelled pyrazoles **146** and **147**.

When compound **49e** reacts with PbO_2 [or with MnO_2, Co_2O_3, NiO(OH)] in MeOH (or EtOH), a two-reaction cascade takes place including oxidation of **49e** to paramagnetic intermediate **36** and the subsequent fast removal of the Me_3Si group.[122,176] In the case of organogermanium compound **145**, cleavage of the Ge–C bond is much slower; therefore, the reaction of **49d** with PbO_2 (or MnO_2) in MeOH for 0.5 h affords nitronyl nitroxide **145** (~75%), which is completely converted to derivative **148** (~75%) only after the oxidation time has been increased to 6 h.[122]

In the ethynyl-substituted nitronyl nitroxide **148**, the electron density of the triple bond decreases due to the strong electron-withdrawing effect of the paramagnetic fragment, which activates the bond towards nucleophilic addition reactions. Conditions for these reactions can be met even in the preparation of **148**; thus it can be introduced in the subsequent reactions without isolation. For example, an increase in the reaction time of $SiMe_3$ derivative **49e** with MnO_2 in MeOH to 24 h affords a mixture of *E*-isomer **149** and *Z*-isomer hydrate **150**·H_2O. If this reaction is carried out in EtOH for 60 h, spin-labelled aminoenal **151** is mainly formed. The use of amine ($BuNH_2$, Et_2NH, Pr^i_2NH) or an EtOH–pyrrolidine mixture as the solvent gives (*E*)-aminovinyl nitronyl nitroxides **152** in high yields (see Scheme 5).

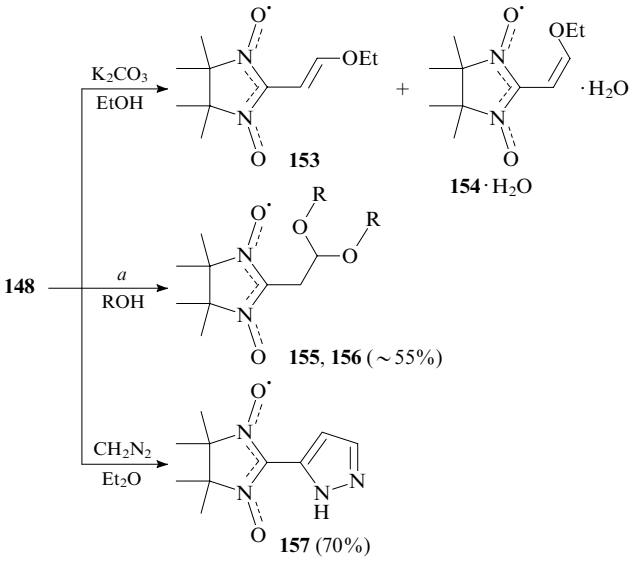
If K_2CO_3 is added to the reaction mixture after completion of the cascade reaction of Me_3Si derivative **49e** with MnO_2 in EtOH or MeOH, a mixture of *E*-isomer **153** and *Z*-isomer hydrate **154**·H_2O or acetal **155** is formed. Unlike the methoxy derivative **150**·H_2O, which firmly holds the water molecule, compound **154**·H_2O is dehydrated during isolation and isomerizes to *E*-isomer **153**. Thus **153** can be obtained in an overall yield of 42%. The addition of KOH

Scheme 5



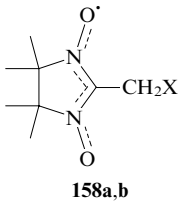
R = $SiMe_3$ (**36**, **49e**, **146**), $GeEt_3$ (**49d**, **145**, **147**).

to solution of **148** in EtOH also results in a mixture of isomers **153** and **154**·H_2O; however, under these conditions, they add one more EtOH molecule at different rates (*E*-isomer is formed much faster) to give diethyl acetal **156**. Compound **148** rapidly reacts with CH_2N_2, unlike organoelement derivatives **36** and **145**, to give only pyrazol-3-yl nitronyl nitroxide **157**.



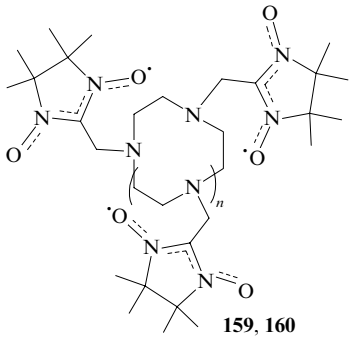
155: R = Me, (*a*) K_2CO_3; **156**: R = Et, (*a*) KOH.

The halogen atom (X = Cl, Br) in XCH_2-substituted nitronyl nitroxides **158a**,**b** is readily replaced on treatment with nucleophiles, which was used to prepare various polynitroxides. Thus the reaction of **158a**,**b** with nitrogen-containing crown compounds affords chelating polyradicals **159**–**161**.[177, 178] By the reaction of **158a** with calix[4]arene in



158a,**b**

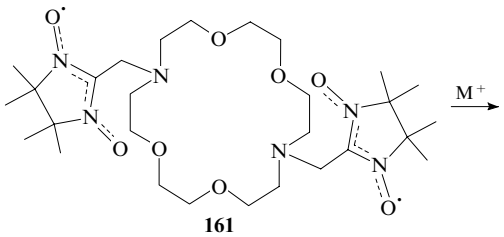
X = Cl (**a**), Br (**b**).



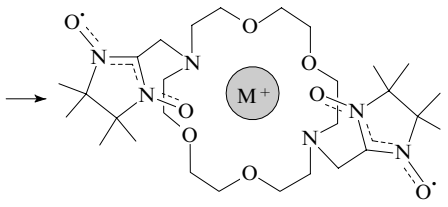
159, **160**

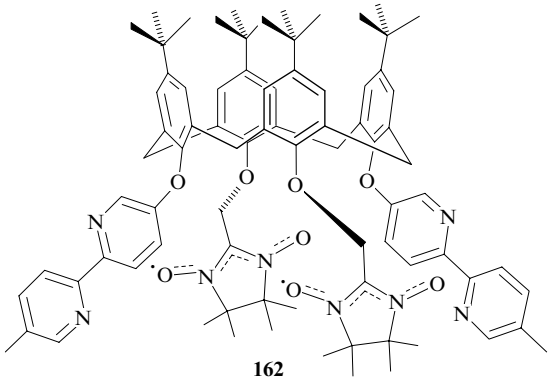
n = 1 (**159**), 2 (**160**).

the presence of catalytic amounts of NaI, a series of calixarene podands and cryptands were obtained.[179] The reaction of these spin-labelled cyclic polydendate compounds with metal ions can result in a change in the distance between the paramagnetic fragments, and, hence, in a particular change in the intramolecular exchange interaction parameters. Thus biradical **161** was found to perform as an active sensor for alkali metal cations with the use of EPR detection and calix[4]arene **162** can serve as a sensor for Zn^{2+} ions.



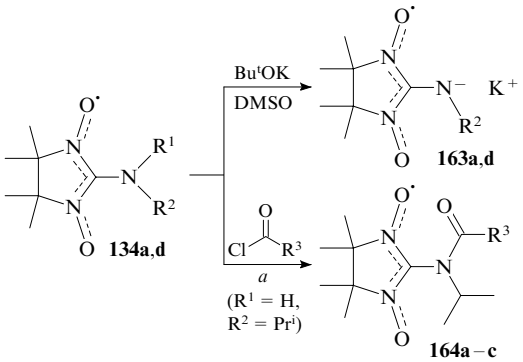
161





162

Against the background of the developed methods for changing the surrounding of the substituent α-carbon atom of nitronyl nitroxides, examples of similar reactions affecting nitrogen-containing substituents are rather scarce. It is known that amino-substituted 2-imidazolin-1-oxyl 3-oxides **134a**,**d** react with KOBu^t in DMSO † to give solutions of the corresponding salts **163a**,**d**; the initial dark brown solution of amine **134a** becomes pale green, and the solution of amine **134d** is decolourized. In the researchers' opinion,[101] this is due to the fact that, according to electronic spectroscopy data, ionization of salts **163a**,**d** induces a shift of the n→π* absorption band from the visible to near IR region. The electronic spectrum of salt **163a** exhibits an absorption



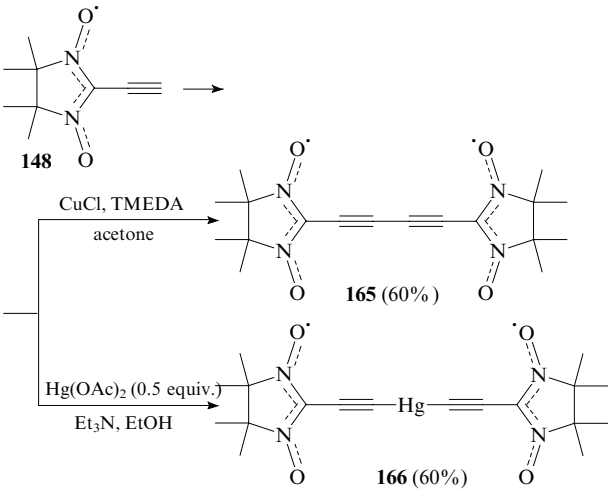
163: R^2 = H (**a**), Pr^i (**d**);

164: R^3 = Me (**a**), Ph (**b**): (*a*) CH_2Cl_2, Et_3N, −20 °C, ~45%;
R^3 = EtO (**c**): (*a*) 2 N NaOH, 60 min, ~20 °C, 19%.

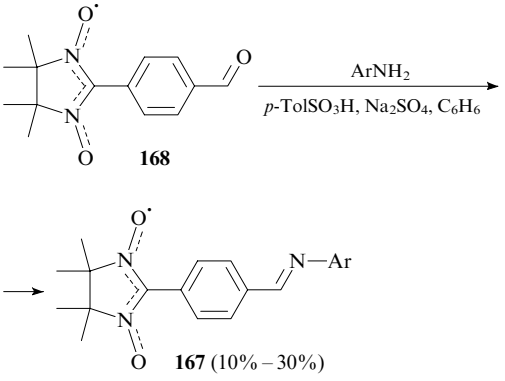
† According to the authors of the publication,[161] the use of DMSO as the solvent should better be avoided in the studies of 2-imidazolin-1-oxyl 3-oxide chemistry and, for example, THF should be employed instead.

band with λ_{max} = 880 nm (ε = 3010) and the spectrum of salt **163d** contains a band with λ_{max} = 995 nm (ε = 2520). By the example of compound **134d**, it was shown that alkylamino-substituted 2-imidazolin-1-oxyl 3-oxides are acylated in the presence of bases to give *N*-acyl-*N*-alkyl derivatives **164a–c**.

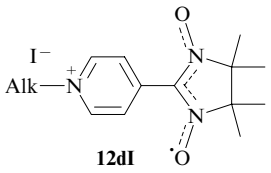
The first example of a reaction changing the surrounding of the β-atom (or more remote atoms) of the substituent was provided by oxidative dimerization of ethynyl nitronyl nitroxide **148** presented below. Dimer **165** was prepared in good yield as it is sparingly soluble in acetone and rapidly precipitates to solid phase after the formation. The reaction of $Hg(OAc)_2$ with ethynyl derivative **148**, similarly to the reaction with unsubstituted nitronyl nitroxide **111**, affords organomercury biradical **166**. Note that biradical **166**, like biradical **115**,[162] may present interest as a ligand. The synthesis of nitronyl nitroxide biradical in whose molecules the diacetylene and paramagnetic nitronyl nitroxide fragments separate additional groups was reported.[180]



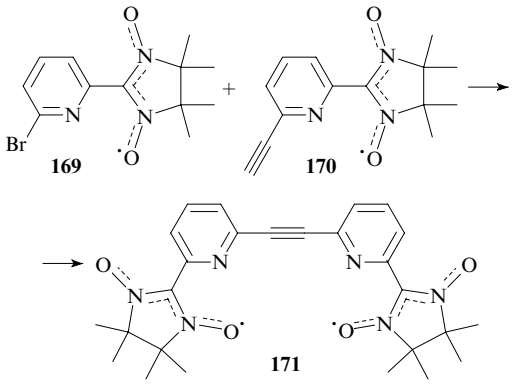
Yet another illustration of the possibilities of synthesis of various nitronyl nitroxides by method 2 is the convergent synthesis of the above-mentioned compounds **20** and **21**. This method proved to be the only possible way, as specially noted by Zhang *et al.*,[181] to prepare Schiff bases **167** by condensation of spin-labelled benzaldehyde **168** with arylamines (80 °C, 4–6 h).



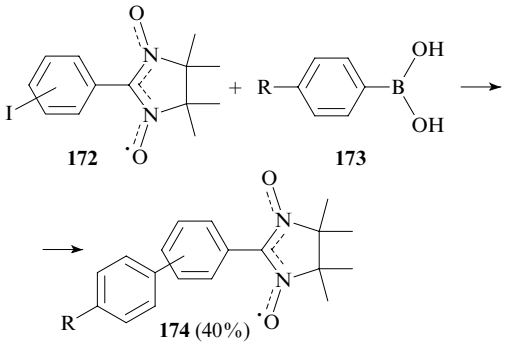
Mention should be made of the reaction of pyridyl-substituted nitronyl nitroxides with AlkI yielding paramagnetic pyridinium salts **12dI**. These compounds undergo exchange reactions with salts containing transition metal complexes as anions. This exchange gives rise to heterospin compounds with diverse magnetic properties.[182, 183] Among these, an outstanding example is the magnet $(\mathbf{12d})_2[Mn_2Cu(opba)_3(DMSO)_2]\cdot H_2O$ [opba is *o*-phenylenebis(oxamate)] with T_C = 22.5 K.[184]



Cross-coupling is still little used in the 2-imidazolin-1-oxyl 3-oxide chemistry, although Romero and Ziessel[185] have demonstrated its high efficiency. They showed that activated nitronyl nitroxide **169** containing 2-bromopyridyl group undergoes the Heck reaction [$Pd(PPh_3)_4$, C_6H_6/Pr^i_2NH] with terminal alkynes. For example, the reaction with spin-labelled alkyne **170** gives biradical **171** (84%).

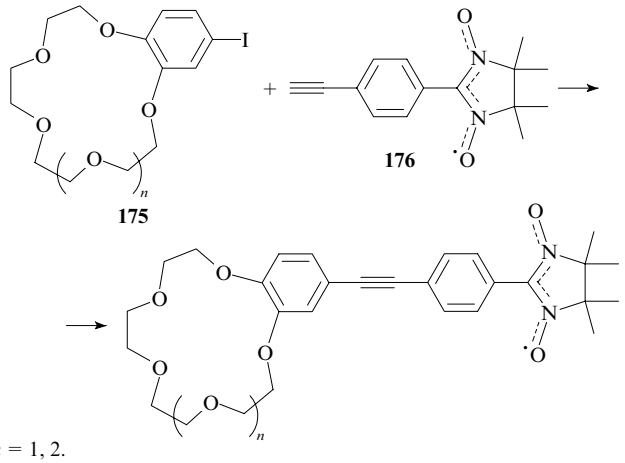


The only example of the Suzuki reaction leading to the cross-coupling products is the reaction of iodo derivatives **172** with arylboronic acids **173** in the presence of $Pd(PPh_3)_4$ and Na_2CO_3 (aq.) (PhMe–MeOH, 1:1, 80 °C, 2–2.5 h) giving radicals **174**.[186]



One of the reasons of rare use of the Sonogashira reaction for cross-coupling is that the nitronyl nitroxides are deoxygenated under conditions of this reaction and the preceding dihydroxyimidazolidines are dehydrated.[187, 188] The successful use of the Sonogashira reaction requires selecting a catalyst system that would ensure proceeding of the reaction at ambient temperature, as at higher temperatures the side process is substantially accelerated. For example, cross-coupling of *m*-diiodobenzene with 2-(3,5-diethynylphenyl)-2-imidazolin-1-oxyl 3-oxide or 4-ethynylbenzonitrile with 3-iodophenyl-2-imidazolin-1-oxyl 3-oxide was accomplished at room temperature in an NEt_3–Py mixture in the presence of $PdCl_2(PPh_3)_2$ and CuI.[189, 190] In

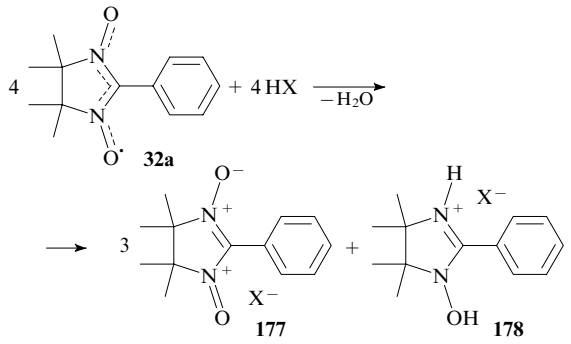
the cross-coupling of 4-iodotoluene, 4-iodobiphenyl, 4-iodoterphenyl and iodinated benzocrown ethers **175** with spin-labelled acetylene **176**, conducting the reaction in piperidine in the presence of $PdCl_2(PPh_3)_2$ and CuI and gradual addition of alkyne **176** to the reaction mixture (1 h) proved to be efficient.[191,192] The product yields were 20%–60%.



175 **176**

n = 1, 2.

Reactions involving 2-imidazolin-1-oxyl 3-oxides are carried out, most often, in neutral or basic media, as in acid media these compounds are unstable. Indeed, on acid treatment of a solution of nitronyl nitroxide **32a**, disproportionation takes place to give salts **177** and **178**. The oxoammonium salt **177** is stable in acid medium but upon the addition of a base it is again converted to NR **32a** but in low yield.[193–195]

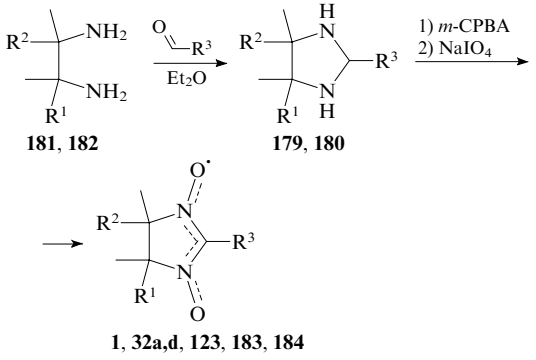


32a **177** **178**

In principle, this type of transformation of nitronyl nitroxides to oxoammonium salts (the theoretical yield is 75%) can be used to protect them for reactions proceeding in acid media because after modification of the 2-substituent in the oxoammonium salt, it can be converted to nitronyl nitroxide by adding a base. Apparently, this protection method is implemented during nitration of compound **32a** or its 4′-fluoro-substituted analogue (65% HNO_3/H_2SO_4, 15 min, 0 → 25 °C) and subsequent alkalification of the reaction mixture, which ends in both cases in the formation of the corresponding 3-nitro derivatives in ~60% yield.[102]

Method 3 implies the oxidation of imidazolidines **179** and **180** obtained by reactions of aldehydes or acetals with vicinal diamines **181** and **182**. The cyclocondensation of diamines with aldehydes occurs in ether at ~0 °C and goes to completion in several minutes (the product yield is ~78%–99%) and the reaction with acetals is carried out in MeOH for 1 h at room temperature and pH 3–4 (the product yields are 67%–78%).

An effective method of oxidation of imidazolidines **179** and **180** comprises two successive reactions carried out as one-pot process. First, a solution of *m*-chloroperbenzoic acid (*m*-CPBA) in CH_2Cl_2 taken in a 2.5-fold excess is added at 0–6 °C to a solution of imidazolidines **179** or **180** in CH_2Cl_2 in the presence of aqueous $NaHCO_3$. The imidazolidine oxidation to 1,3-dihydroxyimidazolidines is completed, most often, in 1 h. The 1,3-dihydroxyimidazolidines thus formed are oxidized to 2-imidazolin-1-oxyl 3-oxides; to this end, another oxidant, *viz*., an aqueous solution of $NaIO_4$, is added to the reaction mixture. The yield of 2-imidazolin-1-oxyl 3-oxides is 65%–80%.

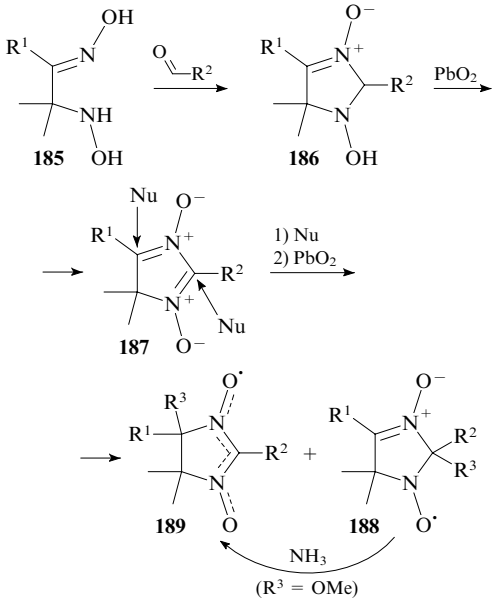


181, **182** **179**, **180** **1**, **32a,d**, **123**, **183**, **184**

$R^1 = R^2$ = Me: R^3 = 4-$NO_2C_6H_4$ (**1**), Ph (**32a**), 3-Py (**32d**), Me (**123**), Bu^t (**183**); $R^1 = R^2$ = Et, R^3 = Ph (**184**).

The synthesis of compound **32d** ($R^1 = R^2$ = Me, R^3 = 3-Py) is accompanied by the side formation of pyridyl *N*-oxide-substituted 2-imidazolin-1-oxyl 3-oxide (8%).[119]

Method 4. In the above methods for preparation of 2-imidazolin-1-oxyl 3-oxides, all substituents R were introduced at the assembly of five-membered heterocycle. According to method 4, first, the 3-imidazoline 3-oxide ring is assembled by the reaction of aldehydes with substituted α-hydroxyamino oximes **185**. Then compounds **186** are oxidized by excess PbO_2 to 4*H*-imidazole 1,3-dioxides



185 **186** **187** **189** **188**

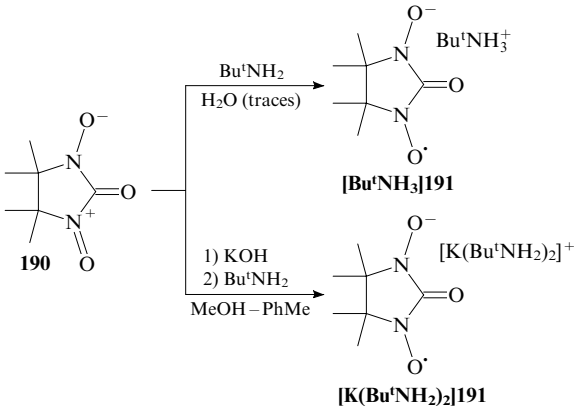
R^1 = Ph, 2-Py; R^2 = Ph, 4-$C_6H_{13}OC_6H_4$, 3-Py; R^3 = OMe, NH_2, NHMe; Nu = MeOH, NH_3, $MeNH_2$.

187; in the presence of active $Pb(OH)_2$, compounds **187** undergo competing reactions of MeOH or amine (NH_3, $MeNH_2$) addition at one of the nitrone fragments incorporated in the ring to give hydroxyimidazolidine *N*-oxides, which are oxidized under reaction conditions to 3-imidazolin-1-oxyl 3-oxides **188** and the corresponding 2-imidazolin-1-oxyl 3-oxides **189**.

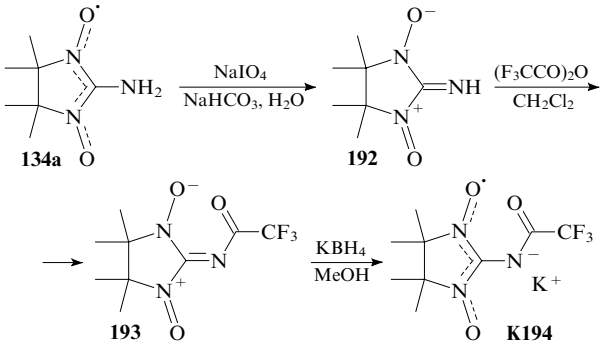
The yield of nitroxides **188** and **189** is determined by the ratio of the addition reaction rates depending, in turn, on the properties of substituents R^1 and R^2 in dioxide **187**. The presence of electron-withdrawing substituent R^1 and electron-donating substituent R^2 or equal R^1 and R^2 favours the formation of 2-imidazolin-1-oxyl 3-oxides **189** (Refs 106 and 196). Using the introduction of the substituents R in different steps, it is possible to carry out targeted synthesis of complex polyfunctional 2-imidazolin-1-oxyl 3-oxides **189**. For example, stirring of dioxide **187** (R^1 = 2-Py, R^2 = 3-Py) with PbO_2 in an ethanol solution of NH_3 for 3–4 h yields nitroxide **189** (R^1 = 2-Py, R^2 = 3-Py, $R^3 = NH_2$) in 56% yield. If the reaction of dioxide **187** (R^1 = 2-Py; R^2 = Ph, 4-$C_{16}H_{33}OC_6H_4$, 3-Py) with PbO_2 is carried out in MeOH, then 2-imidazolin-1-oxyl 3-oxides **189** (R^1 = 2-Py; R^2 = Ph, 4-$C_{16}H_{33}OC_6H_4$, 3-Py; R^3 = OMe) are formed in 60%–75% yields.[197] On treatment with nucleophiles (OH^-, NH_3, NH_2Me), 3-imidazolin-1-oxyl 3-oxides **188** containing an OMe group in position 2 of the imidazoline ring are converted to 2-imidazolin-1-oxyl 3-oxides **189** (R^3 = OH, NH_2, NHMe).[196,198]

The regioselectivity was also observed in the reaction of substituted 4*H*-imidazole 1,3-dioxides **187** with organolithium compounds. Dioxide **187** (R^1 = Ph, R^2 = Me) reacts with excess PhLi to give predominantly the addition product at the phenylnitrone group, isomer **189** ($R^1 = R^3$ = Ph, R^2 = Me). The PhLi addition to dioxide **187** ($R^1 = R^2$ = Ph) and the subsequent oxidation yields both isomeric imino nitroxides, resulting from deoxygenation of nitronyl nitroxide **189** ($R^1 = R^2 = R^3$ = Ph).[123]

Method 5. The reduction of oxoammonium salts can serve as the source of 2-imidazolin-1-oxyl 3-oxides. As an example, consider the zwitter-ion, imidazolidin-2-one 1,3-dioxide **190**, obtained in a moderate yield upon the addition of bromine to a suspension of 2-unsubstituted nitronyl nitroxide **111** in CCl_4 (Ref. 199) or treatment of 2-iodo derivative **132** with 4 N H_2SO_4.[167] The electron affinity of dioxide **190** is rather high [200] and in alkaline media, it is rapidly reduced to give solutions of salts of nitroxide-substituted hydroxamic acid **M191** (M = Na^+, K^+) stable in the absence of oxygen. If a suspension of dioxide **190** is kept in Bu^tNH_2 at ~5 °C, the reduction is completed only after a week to give very thin needle crystals of the ammonium salt **[Bu^tNH_3]191**. In air it is easily oxidized to **190**, because anion **191** has a low [200] oxidation potential. Unlike **[Bu^tNH_3]191**, the salt **[$K(Bu^tNH_2)_2$]191** separates to the solid phase as large single crystals; hence, its oxidation in air is kinetically hampered. This made it possible to carry out X-ray diffraction study of **[$K(Bu^tNH_2)_2$]191** and to establish the geometry of the anion **191**.[199] It was found that the paramagnetic anion is non-planar; the angle between the straight line through the C(4)–C(5) bond and the NCN plane is 16.3°. The nitroxide oxygen lies in the plane of the NCN fragment and the oxygen atom of the deprotonated hydroxyl group deviates from this plane by 0.150 Å. The N–O distance of the nitroxide group is typical of 2-imidazolin-1-oxyl 3-oxides being equal to 1.276 Å; the $N-O^-$ and C=O bond lengths are 1.345 and 1.241(3) Å, respectively.



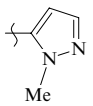
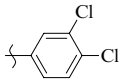
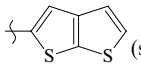
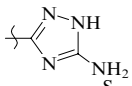
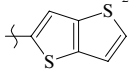
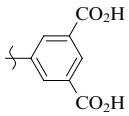
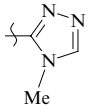
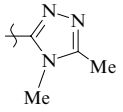
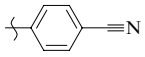
Hydroxamic acid **H191** is unstable, unlike its salts, due to disproportionation to zwitter-ion **190** and the corresponding 1,3-dihydroxyimidazolidin-2-one. The EPR spectrum of acid **H191** was recorded during the electrochemical reduction of zwitter-ion **190** under high dilution (the spectral parameters: a_{N1} = 0.994 mT, a_{N2} = 0.320 mT, a_H = 0.156 mT).[200] The oxidation of 2-amino nitronyl nitroxide **134a** isoelectronic to acid **H191** in the $NaIO_4$, $NaHCO_3-H_2O$ or $PbO_2-CH_2Cl_2$ system affords zwitter-ion **192** (98%). The latter reacts with trifluoroacetic anhydride giving rise to zwitter-ion **193** (61%), which is converted to spin-labelled potassium trifluoroacetamide **K194** on treatment with KBH_4 in the presence of KOH.[101]



Properties and correlations. High stability‡ of, and diversity of synthetic routes to, 2-imidazolin-1-oxyl 3-oxides enabled the synthesis of a broad range of compounds of this class and study of their magnetic-structure relationships. Currently, data on the molecular and crystal structures of more than 300 2-imidazolin-1-oxyl 3-oxides are available.[131] Statistical analysis of these data shows that in solid aryl and hetaryl 2-imidazolin-1-oxyl 3-oxides, the most probable O–N and C(2)–N bond lengths are in the ranges of 1.265–1.295 and 1.335–1.355 Å, respectively. The parameter α characterizing the degree of rotation of the planes of the $O\div N-C=N\rightarrow O$ fragment and the cyclic substituent can acquire values from 0 to 90° (Table 4). In the case of

‡ The term 'stability' is used to mean the kinetic inertness of the compound sufficient for isolation of the compound in a pure state. It should be borne in mind that even on storage in the dark and at low temperature (~5 °C), all 2-imidazolin-1-oxyl 3-oxides gradually lose oxygen being converted to the corresponding 2-imidazolin-1-oxyls at one or another rate.

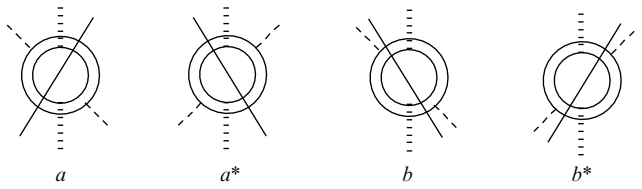
Table 4. Geometric parameters, packing details and exchange parameters for some 2-R-4,4,5,5-tetramethyl-2-imidazolin-1-oxyl 3-oxides.

R	d_{N-O} /Å	$d_{C(2)-N}$ /Å	α /deg [a]	β /deg [b]	Packing details, exchange parameters (J/k /K)	Ref.
	1.279, 1.278	1.340, 1.344	49.0	18.1	dimers; $J/k = -39$ [c]	145
H, α-phase	1.272, 1.276	1.327		16.9	dimers NO···HC(2); $2J/k = -30$ [c]	202
H, β-phase	1.276 – 1.294 [d]	1.316 – 1.333		4.8 – 13.1	dimers NO···HC(2); $2J/k = -22$ [c]	203
	1.271, 1.261	1.351, 1.341	24.2	8.4	chains; $J/k = -8$ [e]	204
 (see [f])	1.281, 1.276 1.275, 1.282	1.355, 1.337 1.365, 1.353	8.7 10.0	0.2 3.3	dimers; $2J/k = -5.2$ [c]	132
	1.283, 1.295 1.276, 1.279	1.356, 1.351 1.350, 1.362	3.7 −10.7	19.0 10.1	H-bonded ribbons; $J/k = -3.6$ [g]	205
	1.279, 1.280	1.352, 1.336	6.3	6.9	chains NO···S; $2J/k = 0.22$	132
	1.286	1.339	47.9	17.8	–	206
	1.276, 1.280	1.336, 1.343	59.4	15.3	1D-chains NO···N_{Het}; $2J/k = 0.6$; weak ferromagnet at $T < 0.6$ K	32
	1.279, 1.273	1.335, 1.342	80.4	11.3	$\theta = 0.45$ [h]; ferrimagnet $T_N = 0.33$ K	207
	1.274, 1.275	1.340, 1.340	89.2	0.4	quasi-3D-lattice; $\theta = 0.48$ K;[h] ferromagnet $T_C = 0.3$ K	208
	1.257 1.270	1.354 1.343	16.2 33.0	7.8 17.7	quasi-square lattice; $J/k = 0.75$ [i]	209
	1.284, 1.283	1.336, 1.338	28.7	11.5	1D-stacks; $J/k = 18.2$ [j]	210
	1.267	1.318		0.0	layers; $J/k = -14$ [k]	171
	1.266, 1.269	1.338, 1.331		14.7	chains C≡CH···ON; weak AF interactions	see [l]
	1.271, 1.280	1.335, 1.331	90.6	11.0	molecular	166

[a] Dihedral angle between the plane of the ONCNO fragment and the plane of the aromatic ring of the substituent R. [b] Angle between the straight line through the C(4) – C(5) atoms in the imidazoline ring and the ONCNO plane. [c] Dimer model. [d] Three different dimers. [e] Antiferromagnetic chain model. [f] Two independent molecules. [g] Alternating chain model. [h] the Curie – Weiss law. [i] 2D-Ferromagnet model. [j] Model of ferromagnetic chain of spins with $S = {}^1/_2$. [k] Model of antiferromagnetic square 2D-lattice of spins with $S = {}^1/_2$. [l] Our data.

great α values, the π-conjugation between the rings is disturbed; this induces a hypsochromic shift of the long-wavelength absorption band in the UV spectra. Whereas the long-wavelength absorption maximum in the UV spectra of aryl-substituted nitroxides with $\alpha \leqslant 50^\circ$ is in the range of 630 – 680 nm, in the spectrum of 4,8-dimethoxy-5-formyl-naphth-1-yl-substituted NR with α of 81°, this band occurs at 566.5 nm and the compound is dark red coloured in both solution and the solid phase.[201]

Veciana and co-workers [211] noted a peculiar effect, in particular, the crystals of aryl-substituted 2-imidazolin-1-oxyl 3-oxides are composed much more often of enantiomer pairs with pseudoeclipsed (*b*,*b**) than with pseudo-*anti*-conformation (*a*,*a**; Fig. 3).[211] Thus it is possible to crystallize one of the four conformers by introducing a chiral group into a paramagnetic 2-aryl-2-imidazolin-1-oxyl 3-oxide molecule.[147, 212, 213] Paramagnetic crystals with an *R*-lactate group in position 4 of the phenyl substituent



—— bond C(4)—C(5), ''''' fragment ONCNO,
--- aromatic ring.

Figure 3. Schematic view of diastereomers of aryl-substituted 2-imidazolin-1-oxyl 3-oxides with pseudoeclipsed (*b*,*b**) and pseudo-*anti* conformations (*a*,*a**).

formed by molecules in the pseudoeclipsed *b*-conformation were obtained. In the crystals of a racemic mixture, the molecules with *R*-lactate group have a pseudoeclipsed *b*-conformation and those with *S*-lactate group have a pseudoeclipsed *b**-conformation. This is important knowledge because magnetic properties of the solid phases of enantiomerically pure paramagnet and its racemic mixture are different.[212]

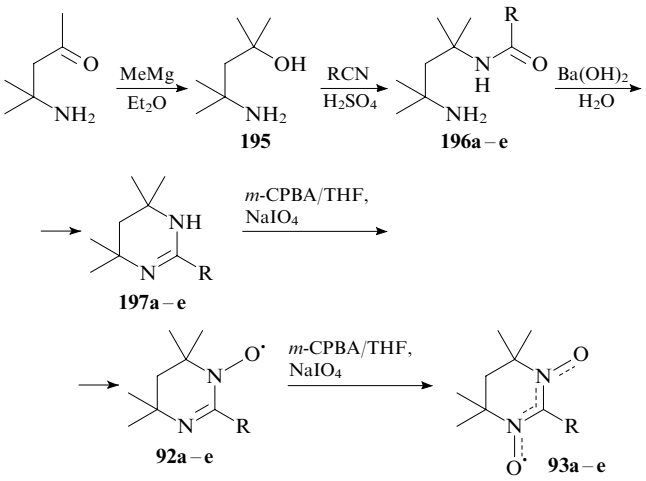
Valuable information was gained from a polarized neutron diffraction study of a single crystal of NR **32a**, which demonstrated that the spin density is mainly localized within an NR molecule in the p-orbitals of the NO-group nitrogen or oxygen. In the NO group, the spin density is equally distributed between the O (0.27) and N (0.27) atoms. The negative spin occupancy of the C(2) atom equal to −0.121 predetermines the spin density alternation pattern (+/−/+/−) in the benzene ring.[214] The found spin density values and signs in the benzene ring are in good agreement with those for NR **32a** found by ^{1}H and ^{13}C NMR spectroscopy.[215,216]

Generally, the magnetic properties of solid phases of nitronyl nitroxides (see Table 4) are determined by the system of numerous intermolecular contacts involving the ONCNO fragment that form an intricate network of exchange channels.[26,27]

b. 1,4,5,6-Tetrahydropyrimidin-1-oxyl 3-oxides

A number of methods of synthesis of 1,4,5,6-tetrahydropyrimidin-1-oxyl 3-oxides **93** have been developed. In **method 1**, the key step is the Ritter reaction of amino alcohol **195** with excess nitrile ending in the formation of amino amides **196**, which then cyclize in the presence of a base to 1,4,5,6-tetrahydropyrimidines **197** (Scheme 6).[217] The oxidation of **197** affords nitroxides **93**. This reaction, like oxidation of imidazolidines **179** and **180** (see Scheme 4, method 3), can be arrested after the formation of imino nitroxides — 1,4,5,6-tetrahydropyrimidin-1-oxyls **92**.

Scheme 6

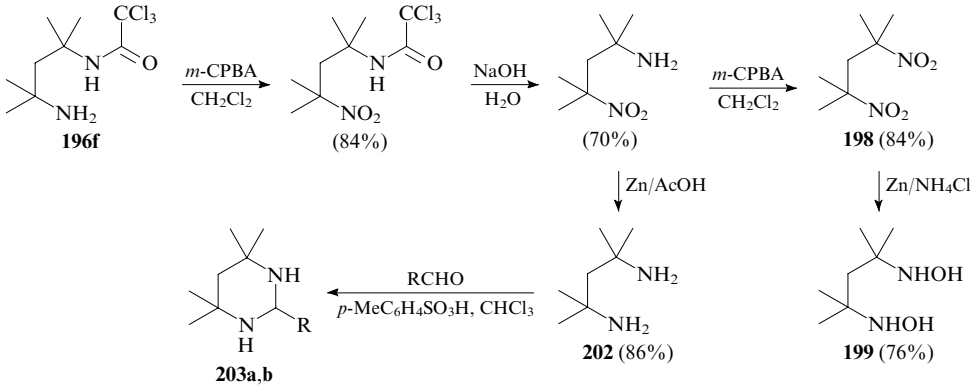


R = *p*-$NO_2C_6H_4$ (**93a**, 60%), Ph (**93b**, 40%), *p*-$MeOC_6H_4$ (**93c**, 40%), 3-Py (**93d**, 30%), Me (**93e**, 10%).

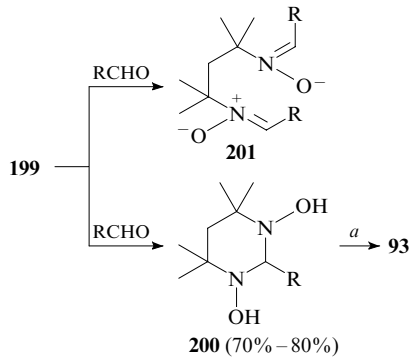
Method 2 requires preliminary transformation of compound **196f** (R = CCl_3) to dinitro derivative **198**, which is then reduced to 2,4-bis(hydroxyamino)-2,4-dimethylpentane (**199**) (Scheme 7).

The condensation of compound **199** with formaldehyde or acetaldehyde is carried out in $CHCl_3$ at 25 °C; in the case of aromatic aldehydes, the reaction is carried out at 60 °C in the presence of catalytic amounts of *p*-$MeC_6H_4SO_3H$ or pyridinium *p*-toluenesulfonate. The reaction giving 1,3-dihydroxypyrimidines **200** smoothly proceeds upon gradual (during 5 h) introduction of a carbonyl compound to the reaction mixture. The subsequent oxidation of **200** affords nitronyl nitroxides **93** in good yields provided that an appropriate reagent has been selected. If the aldehyde is added in one portion, as in the synthesis of 1,3-dihydroxyimidazolidine, bis-nitrone **201** is formed. The preparation of compounds **93** through diamine **202** is hampered by the low yield **93** in the oxidation step of hexahydropyrimidines **203** (see Scheme 7).[133]

Scheme 7



R = Me (**203a**, 76%), *p*-$NO_2C_6H_4$ (**203b**, 65%).



R = H, Alk: (*a*) $NaIO_4/CH_2Cl_2$, $NaHCO_3$ (aq.) (50% – 60%);
R = Ar, Het: (*a*) *m*-CPBA (60% – 70%).

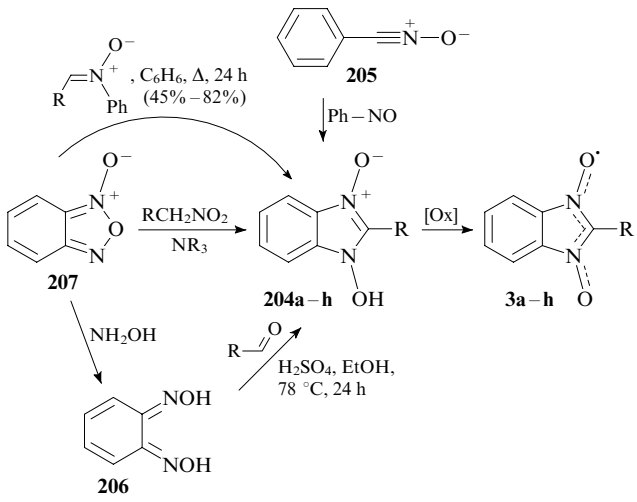
Properties and correlations. 2-Aryl-substituted NR **93**, like related 2-imidazolin-1-oxyl 3-oxides, are dark violet crystals. The similarity of the colour of these compounds is supported by the data of visible absorption spectra for **93b** [λ_{max} (ε) = 626 nm (935)] and **32a** [λ_{max} (ε) = 587 (407), 637 nm (450)] recorded under identical conditions. The constants a_N lie in the range of 0.710 – 0.712 mT (toluene) for 2-aryl-substituted derivatives **93** and in the range of 0.720 – 0.724 mT for alkyl-substituted compounds, *i.e.*, they are approximately 0.03 mT lower than those in 2-imidazolin-1-oxyl 3-oxides with similar substituents in position 2. An X-ray diffraction study of solid NR **93** has shown that the paramagnetic fragment ONCNO is nearly planar. The average O – N and N – C(2) bond lengths in this fragment are close to those in 2-imidazolin-1-oxyl 3-oxides being equal to 1.287 and 1.350 Å. The racemic crystals of **93**, like the crystals of 2-imidazolin-1-oxyl 3-oxides, are built of pairs of optically active conformers formed upon the opposite rotation of the ONCNO fragment with respect to the rest of the heterocycle. The molecules of aryl-substituted derivatives **93** acquire preferably a pseudoeclipsed conformation (*b*,*b**, see Fig. 3), which has much greater angles between the plane of the ONCNO fragment and the plane of the aromatic ring than 2-imidazolin-1-oxyl 3-oxides.[133]

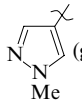
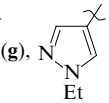
c. Benzoimidazol-1-oxyl 3-oxides

The $O \dot{-} N - A^2Y$ fragment is also present in benzoimidazol-1-oxyl 3-oxides **3**, which have long been classified as short-lived radicals. It was considered that they can hardly be isolated.[218] However, development of synthetic methods allowed the synthesis of some of them. They were even grown as single crystals and the magnetic-structural relationships were investigated.

The preparation of crystals **3e** requires a specific procedure for oxidation of derivative **204e**: a suspension of **204e** and PbO_2 is stirred for 10 min in CH_2Cl_2, after that the mixture of PbO_2 and the unchanged **204e** poorly soluble in CH_2Cl_2 is filtered off. As a result, the contact time of NR **3e** with the oxidant is minimized. This procedure repeated several times produces good-quality **3e**, which can be additionally purified and obtained as single crystals by recrystallization from n-alkane.[219] This method also proved efficient in the preparation of crystalline polyhalophenyl- (**3a** – **d**), 3-cyanophenyl- (**3f**) (see Ref. 19) and *N*-alkylpyrazolyl-substituted (**3g**,**h**) nitroxides (Scheme 8).[220]

Scheme 8



R = 2,6-$F_2C_6H_3$ (**a**), 2,3,6-$Cl_3C_6H_2$ (**b**), 2,6-$Cl_2C_6H_3$ (**c**), C_6F_5 (**d**), Ph (**e**), 3-NCC_6H_4 (**f**),  (**g**),  (**h**).

In some cases, oxidation of nitrones **204** is carried out using aqueous $NaIO_4$,[219] for example, in the case of 1-hydroxy-2-(4-azidophenyl)benzoimidazole 3-oxide, the process is carried out for 15 min, and then CH_2Cl_2 and aqueous $NaHCO_3$ are added, the product is extracted to the organic phase (~40%).[221] Silver(I) triflate is a convenient oxidant, which allows nitrones **204** to be converted to nitronyl nitroxides **3** under mild conditions; this oxidant is added to a solution of tetrabutylammonium salt of deprotonated compound **204** in toluene under sonication.[222]

The starting nitrones **204** were prepared by condensation of benzonitrile oxide (**205**) with nitrosobenzene, acid-catalyzed condensation of dioxime **206** with aldehydes or by the reaction of benzofuroxan **207** with primary nitroalkanes or arylnitrones (see Ref. 222 and references cited therein).

Properties and correlations. The isolated 2-aryl and 2-hetaryl nitronyl nitroxides **3** are coloured greenish-brown of different tints. A specific feature of the electronic spectra of compounds **3** (in MeCN) is the presence of a broad absorption band at ~760 – 970 nm (ε = 260 – 1200) with a maximum in the near-IR region. Simulation of the EPR spectra of solutions of 2-aryl-substituted derivatives **3** in benzene gave g-factors of 2.0069 ± 0.0003. The HFC constants a_N are in the range of 0.43 – 0.44 mT, while the HFC constants a_H for α- and β-proton pairs in the annulated benzene ring are in the ranges of 0.0091 – 0.008 and 0.0065 – 0.0072 mT, respectively. The values of HFC constants a_N and a_H attest to pronounced spin density delocalization (~10%) in the imidazole fragment to the annulated benzene ring.

A study of the electrochemical behaviour of 2-phenylbenzoimidazol-1-oxyl 3-oxide (**3e**) (solvent MeCN) has shown that it undergoes reversible single-electron reduction at 0.001 V *vs*. the standard calomel electrode and reversible oxidation at 1.61 V. The replacement of the phenyl group by the β- or α-thienyl group results in a decrease in the reduction potential $E_{1/2}$(Red) to 0.02 and 0.03 V, respec-

tively, and replacement by the γ-pyridyl group gives rise to irreversible reduction at $E_{an}(Red) = -0.2$ V. Thus, radicals **3** are better electron acceptors than, for example, radical **32a**, which undergoes reversible single-electron reduction at −0.741 V and reversible single-electron oxidation at 1.00 V under the same conditions.

According to X-ray diffraction analysis, the 1-oxylbenzoimidazole 3-oxide core has a planar structure, the range of O−N bond lengths is 1.27–1.29 Å, and N−C(2) bond lengths are in the range of 1.35–1.36 Å, which overlaps the limits of variation of these geometric parameters in 2-imidazolin-1-oxyl 3-oxides. In aryl-substituted derivatives **3**, the angle between the plane of the benzene ring and the ONCNO plane, which is 10.3° for R = Ph, increases upon the replacement of hydrogen atoms in the phenyl ring by halogen atoms to reach 66.1° for R = 2,6-$Cl_2C_6H_3$. The rotation of the substituent R relative to the benzoimidazole ring prevents stacking in the packing of NR **3b** and **3c**. As a consequence, dimers are formed instead of stacks (Figs 4 and 5).

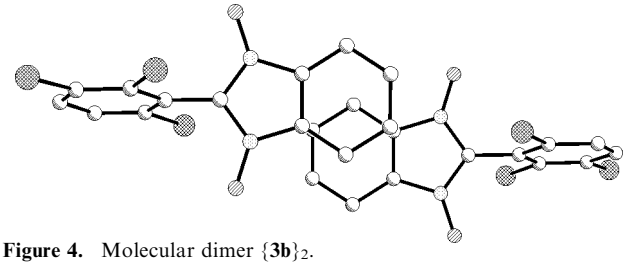


Figure 4. Molecular dimer $\{\mathbf{3b}\}_2$.

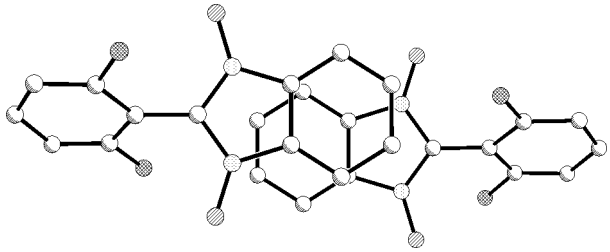


Figure 5. Molecular dimer $\{\mathbf{3c}\}_2$.

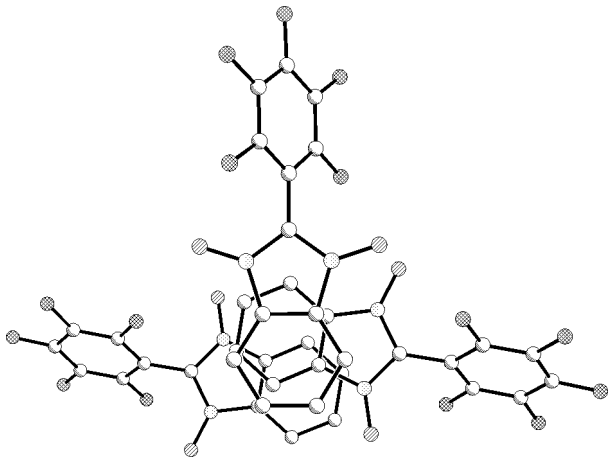


Figure 6. Packing fragment of **3d**.

The formation of stacks in the crystal structure of **3d** required helical packing of molecules, which helps to avoid inadmissible overlap between the atoms of fragments R (Fig. 6).

The replacement of the six-membered aryl substituent by a five-membered hetaryl (pyrazolyl) fragment decreases the steric interaction between the rings; as a result, in pyrazolyl-substituted derivatives of **3g**,**h**, the benzoimidazole and pyrazole rings are coplanar (Figs 7 and 8).[220]

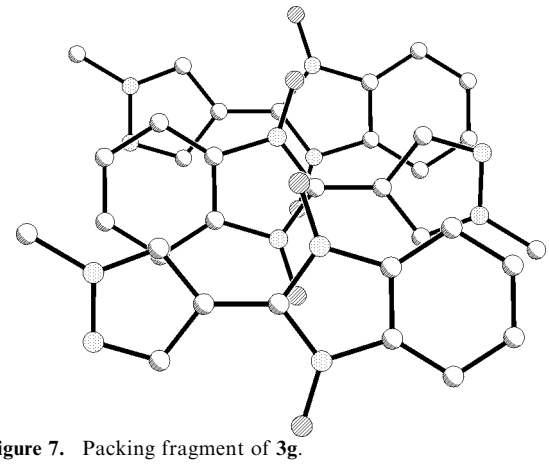


Figure 7. Packing fragment of **3g**.

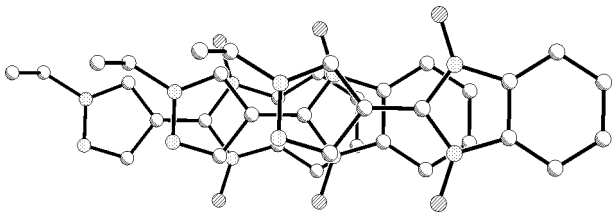


Figure 8. Packing fragment of **3h**.

The planar structure and spin density delocalization of the benzoimidazole NR promote the formation of channels in solid compounds **3** providing rather strong exchange interactions between the unpaired electrons (Table 5).

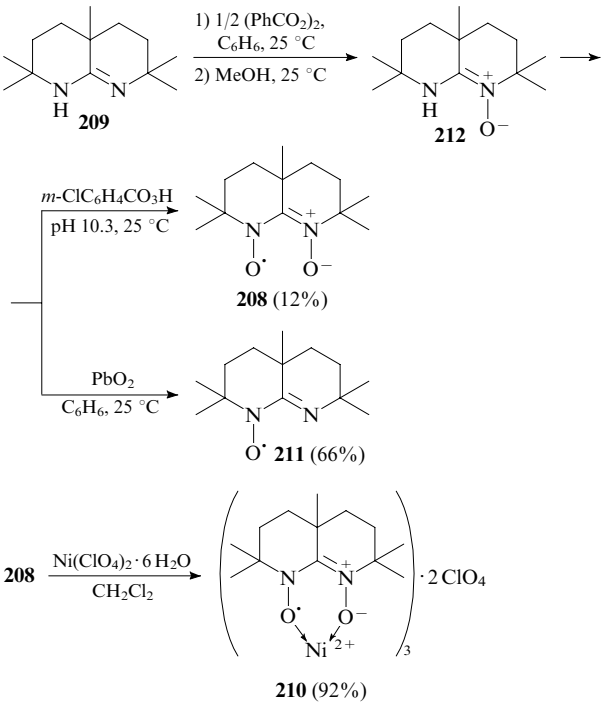
Table 5. Magnetic properties of benzoimidazol-1-oxyl 3-oxides **3**.

Substituent R	Magnetic properties		μ_{eff} at 300 K /μ_B	Ref.
	J/k /K	J'/k [a] /K		
3-NCC_6H_4	−95 [b]		1.28	19
2,6-$Cl_2C_6H_3$	−84 [b]		1.55	19
Ph	∼−40 [b]	−10	1.73	219
C_6F_5	$\theta = -37$ [c]		1.52	19
4-(1-MePz)	−80		1.73	see [d]
4-(1-EtPz)	0.6 [e]		1.73	220
2,6-$F_2C_6H_3$ (α)	66 [e]	−14	1.52	19

Pz is pyrazolyl. [a] J'/k is the intercluster exchange interaction parameter. [b] Dimer model. [c] The Curie–Weiss law. [d] Our data. [e] Chain model.[223]

d. 1,2,3,4,4a,5,6,7-Octahydro-1,8-naphthyridin-1-oxyl 8-oxide

A fundamentally different structural topology of the $O\dot{-}N-A^2O$ fragment was implemented in 2,2,4a,7,7-pentamethyl-1,2,3,4,4a,5,6,7-octahydro-1,8-naphthyridin-1-oxyl 8-oxide (**208**), which can be useful in the design of new structural types of magnets. The synthesis of compound **208** comprises the assembly of the bicyclic amidine **209** and its subsequent specific two-step oxidation. The cyclic voltammetry curve of NR **208** exhibits a reversible wave with $E_{1/2}(Ox) = +0.73$ V (a 0.1 N calomel electrode as the reference electrode) and an irreversible wave with $E_{an}(Red) = -1.45$ V. In the visible region, a solution of NR **208** in EtOH absorbs at $\lambda = 591$ nm ($\varepsilon = 330$). An equivalent electron density distribution among the N–O groups is indicated by the HFC constant $a_N = 0.764$ mT (CH_2Cl_2).[224]



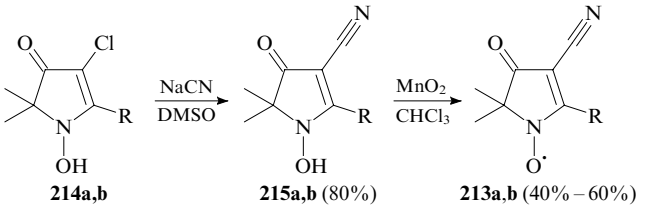
It was shown that coordination of NR **208** by metal ions results in chelates **210**. It cannot be ruled out that the same coordination mode can be inherent in metal complexes with imino nitroxide **211** obtained upon oxidation of nitrone **212**. An essentially asymmetric distribution of the unpaired electron in the $O\dot{-}N-C{=}N$ fragment in imino nitroxide **211** is indicated by the HFC constants ibserved in the EPR spectrum (CH_2Cl_2): $a_{N(1)} = 1.18$, $a_{N(2)} = 0.24$ mT. For radical **211**, the reversible wave was observed at $E_{1/2}(Ox) = +1.02$ V (*vs.* the calomel electrode) and the irreversible wave occurred at $E_{an}(Red) = -1.3$ V.

3. Nitroxides $O\dot{-}N-A^3Y$

a. 3-Cyano-4-oxo-2-pyrrolin-1-oxyls

Monocyclic nitroxides with an $O\dot{-}N-A^3Y$ fragment are represented at the Cambridge Crystallographic Data Centre only by substituted 3-cyano-4-oxo-2-pyrrolin-1-oxyls **213**. This group of compounds can also be considered as both vinylogues of carbonyl nitroxides **99** (structural type $O\dot{-}N-C^3O$) and 2-cyanovinyl nitroxides (structural type $O\dot{-}N-C^3N$), because according to EPR data, the electron spin density in compound **213a** is effectively delocalized from the nitroxide group to the nitrile group: $a_N(N-O) = 0.60$, $a_N(C{\equiv}N) = 0.10$ mT.[225] The synthesis of 2-substituted derivatives **213** starts from the corresponding 3-chloro-1-hydroxy-4-oxo-2-pyrrolines **214** in which the halogen atom can be exchanged under mild conditions (20 °C, 45 min) with a nitrile group to give diamagnetic precursors **215**.[225]

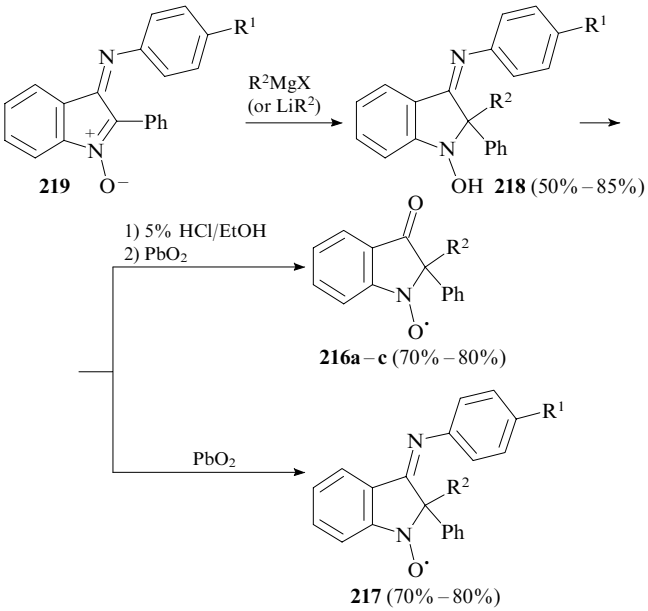
Of interest are the magnetic properties of NR **213a**, where antiferromagnetic exchange chains with $|J/k| = 101$ K are formed in the solid phase.



R = Ph (**a**), 3-Py (**b**).

b. 3-Oxoindolin-1-oxyls and 3-(arylimino)indolin-1-oxyls

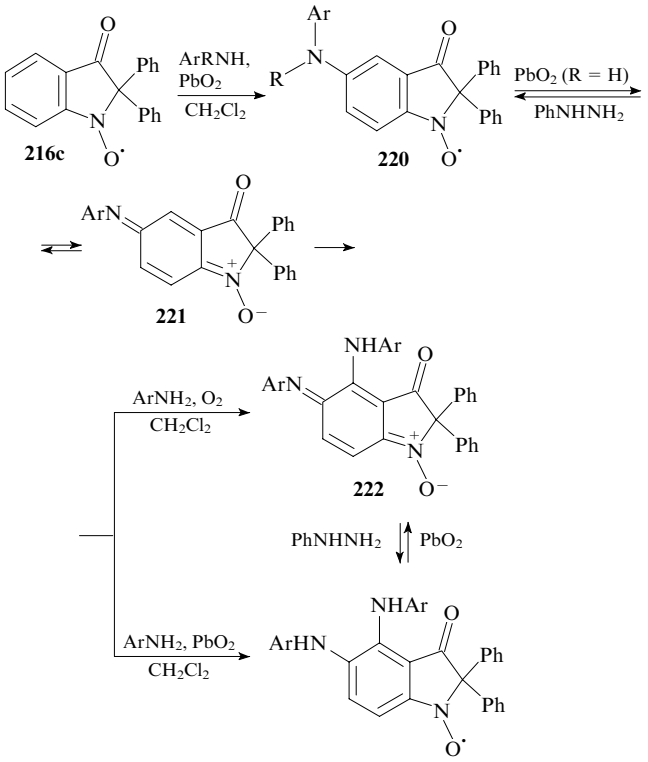
Among bicyclic nitroxides of the $O\dot{-}N-A^3Y$ type, substituted 3-oxoindolin-1-oxyls **216** and related 3-(arylimino)indolin-1-oxyls **217** in which the double bond of the fragment A^3 is a part of aromatic system are sufficiently stable for isolation of the paramagnetic species in a free state. Nitroxides **217** are obtained in good yields by PbO_2 oxidation of the corresponding hydroxyl derivatives **218**, which are, in turn, formed upon the reaction of 2-phenyl-3-aryliminoindolenine *N*-oxides **219** with Grignard reagents or organolithium compounds. The use of compounds **218** also underlies an effective method for the preparation of NR **216**, which comprises hydrolysis of **218** to 1-hydroxyindolin-3-ones followed by their oxidation.[226, 227]



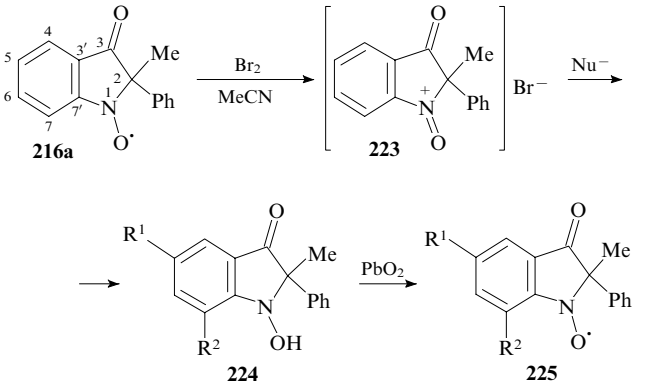
216: R^2 = Me (**a**), Et (**b**), Ph (**c**);
217: R^1 = H: R^2 = Ph, Bn, Et, Pr^i, Bu^t;
R^1 = OMe: R^2 = Ph, Bn, Et.

For **216**, reactions in which the $O\dot{-}N-C{=}C-C{=}O$ fragment remains intact or can be readily regenerated have been described. Thus it was shown that 3-oxo-2,2-diphenylindolin-1-oxyl (**216c**) is aminated in the presence of excess PbO_2 giving rise, in the case of secondary aromatic amines,

to stable 5-substituted 3-oxoindolin-1-oxyls **220**. Analogous compounds are also obtained when primary aromatic amines are used; however, in the presence of PbO_2, they are oxidized to 3-oxo-2,2-diphenyl-5-(arylimino)-3,5-dihydro-2*H*-indole 1-oxides **221**, which can react under reaction conditions with one more amine molecule, which results in gradual accumulation of the corresponding aminated quinonediimine *N*-oxide **222** in the reaction mixture. In the absence of PbO_2, indole 1-oxides **221** react with amines in CH_2Cl_2 also to give products **222**.[228]



The action of bromine on NR **216a** induces its oxidation to oxoammonium salt **223**, and, hence, the electrophilicity of the aromatic ring increases. This facilitates the nucleophilic attack on the unsubstituted carbon atoms of the ring, which ends in the formation of the products of hydrogen nucleophilic substitution, namely, cyclic hydroxyamines **224**. The oxidation of **224** yields 3-oxoindolin-1-oxyls **225**.[229]



$Nu^- = Br^-, AcO^-, PhCO_2^-$;
224, **225**: $R^1 = Nu, R^2 = H$; $R^1 = H, R^2 = Nu$.

3-Oxoindolin-1-oxyls are involved in homolytic substitution with retention of the paramagnetic fragment. For example, their reactions with $(ArCO_2)_2$ or $ArCO_3H$ gives a mixture of 5- and 7-aroyloxy derivatives in a low yield, the latter being the major component. Although the yields are very low, it is important that the substitution still occurs. The ratio between the 5- and 7-substitution changes to the opposite one in the reaction of **216** with the $Bu^tO^{\bullet}$ radical generated in the $Bu^tO_2H - FeSO_4 - MeCN$ system, and their overall yield of ~50%–70% becomes admissible for a preparative synthesis.[230] Later,[231] it was shown that in the $Bu^tOH - PbO_2$ – acetone system, 3-oxoindolin-1-oxyls and 3-phenyliminoindolin-1-oxyls undergo similar homolytic substitution reactions.

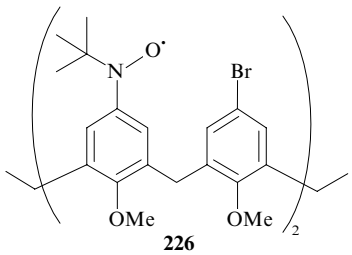
Properties and correlations. Nitroxides **216** and **217** are deep-red coloured. A study of the EPR spectra of benzene or CCl_4 solutions of **216** and **217** showed that typical HFC constants a_N are in the range of 0.92–0.96 mT. This means that the electron spin density within the molecules is effectively delocalized over the indolinone system, which is confirmed by the variation ranges of HFC constants a_H and a_N for compound **217**: a_H[5(7)-H] = 0.29–0.33, a_H[4(6)-H] = 0.10–0.11 and a_N(C=N) = 0.070–0.079 mT. According to X-ray diffraction,[232,233] the N÷O bond lengths in 3-oxoindolin-1-oxyls are in the range of 1.250–1.262 Å, the N–C(7′) bonds are 1.398–1.428; the C(7′)–C(3′) bonds are 1.395–1.398, the C(3′)–C(3) bonds are 1.423–1.439 and the C(3)=O bonds are 1.230–1.243 Å.

4. Nitroxides of the O÷N–A^{n}Y group at $n > 3$

The syntheses of aryl-substituted *tert*-butyl nitroxides of the O÷N–A^{n}Y group, where $n > 3$, were developed mainly for the subsequent use in the synthesis of heterospin complexes with paramagnetic metal ions.[234] In addition, *tert*-butyl nitroxides of this group with Y = NH or OH are able to form intermolecular H-bonds, which makes them even more attractive as components of the controlled assembly of high-dimension systems.

Aryl-*tert*-butyl nitroxides are obtained, like 2-hetaryl-*tert*-butyl nitroxides (see Table 2), by the reaction of organolithium compounds with 2-methyl-2-nitrosopropane with subsequent oxidation of *N*-*tert*-butylhydroxylamines with PbO_2. 4-(1*H*-1,2,4-Triazol-1-yl)phenyl-*tert*-butyl nitroxide,[235] 4-(1*H*-benzoimidazol-2-yl)phenyl-*tert*-butyl nitroxide,[135] 4-(*N*-*tert*-butyl-*N*-oxylamino)benzoic acid[236] and 4-(*N*-*tert*-butyl-*N*-oxylamino)-1,1′-biphenyl-3′,5′-dicarboxylic acid were synthesized in this way.[237] All these NR were prepared as single crystals and the role of H-bonds in the packing was studied.

Calix[4]arene **226** with two Bu^t–N(÷O) groups at the upper rim was prepared; heating of this compound induces the transformation of the calix[4]arene molecule from the partial cone conformation to 1,2-alternate conformation (with respect to the MeO substituents).[238] This structural



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reorganization of the biradical appreciably modulates its EPR spectrum, and this makes it possible to follow the process dynamics.

Usually *tert*-butyl nitroxides are unstable and decompose on attempted isolation. However, upon reactions with metal ions in solution, these NR can form solid complexes stable under ordinary conditions. This method was used to prepare heterospin coordination compounds with 4- and 3-pyridyl-,[239] 2,2′-bipyridin-4-yl-*tert*-butyl nitroxides[240] and with 4-(1*H*-imidazol-1-yl)phenyl-[239] and 4-(pyridin-3-yl)phenyl-*tert*-butyl nitroxides.[241] A number of spin-labelled complexes with diamagnetic metal ions were obtained by the reaction of AuCl, $PdCl_2$, $[(\eta^3\text{-}C_3H_5)PdCl]_2$ or $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ with 4-(diphenylphosphino)-phenyl-*tert*-butyl nitroxide.[242,243]

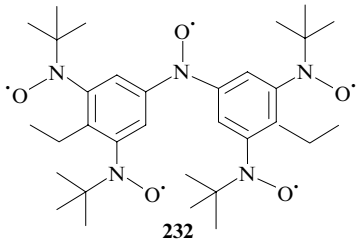
Di-*p*-anisyl nitroxide, the first structurally characterized (1953) stable NR, also belongs to this group of NR.[244,245] Later, a series of *N*-aryl-*N*-(4-pyridyl) nitroxides were synthesized by oxidation of appropriate hydroxylamines with Ag_2O in ether; the yields of the paramagnetic compounds were 60%–80%. *N*-Aryl-*N*-(4-pyridyl) nitroxides with Ar = 2,4,6-$Ph_3C_6H_2$ and 2,4,6-$Bu^t_3C_6H_2$ were obtained as high-quality crystals; hence, their molecular and crystal structures were determined by X-ray diffraction. *N*-Aryl-*N*-(4-pyridyl) nitroxides react with $Co(NCS)_2$ to give heterospin complexes among which antiferromagnets with $T_N < 4.8$ K and, which is of particular interest, single-metal single-molecular magnets with rather high U_{eff} reaching 48 K were found.[246] Using the accumulated experience of working with *N*-aryl-*N*-(4-pyridyl) nitroxides, Koga and co-workers[247] were able to prepare *N*,*N*-di(pyridyl) nitroxide and make it to react with paramagnetic metal ions resulting in chain-polymeric and layer-polymeric heterospin complexes.

5. Polynitroxides $O^{\cdot}\!-\!N\!-\!A^n(N^{\cdot}\!-\!O)_x$

Currently, the synthesis of diverse π-conjugated polynitroxides in which *N*-oxylamino-, *N*-*tert*-butyl-*N*-oxylamino-, 1-oxyl-4,4,5,5-tetramethylimidazolin-2-yl 3-oxide and 1-oxyl-4,4,5,5-tetramethylimidazolin-2-yl groups in various combinations function as paramagnetic fragments has been developed. Since general methods for the introduction of such groups were discussed above, here we consider only the characteristic features of synthesis of paramagnetic molecules with nitroxide groups of different nature.

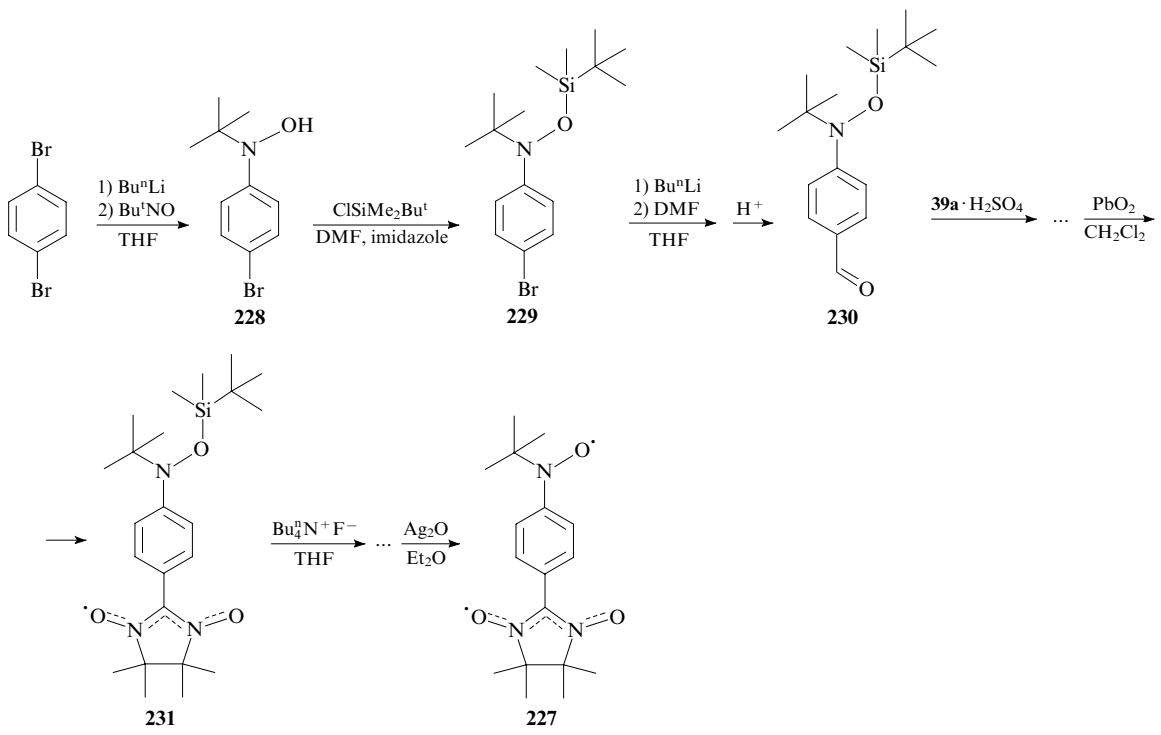
In the synthesis of biradical **227** from bromo derivative **228**, the N–OH group was first protected (derivative **229**). This made it possible to perform all of the necessary steps: from the synthesis of aldehyde **230** to monoradical **231**. Then the protecting group was removed and the resulting unstable hydroxyamino derivative was oxidized to biradical **227**, which was isolated as stable dark violet crystals (Scheme 9).[248]

In the synthesis of diaryl nitroxides, for example, triradical **25**,[105] a solution of 4-bromophenyllithium in THF was treated with isopentyl nitrite at −80 °C and then with Bu^tMe_2SiCl in the presence of Et_3N at room temperature. After chemical transformation of bromine atoms to paramagnetic substituents, the protecting group was removed, and in the final step, the NOH group was oxidized to the nitroxide group. Pentanitroxide **232** was obtained using analogous synthetic approaches[249]



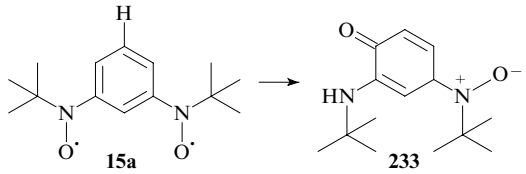
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Scheme 9



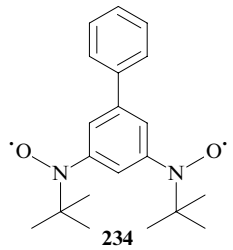
228 **229** **230** **231** **227**

Properties and correlations. 1,3-Phenylenebis(*tert*-butyl nitroxide) **15a** has a high-spin ground state with the exchange interaction energy $2J/k \gg 300$ K.[73,75,250,251] Radical **15a** is unstable; both in solution and in the solid phase, it is spontaneously converted in several hours to isomeric 3-(*tert*-butylamino)-*N*-*tert*-butyl-l,4-benzoquinoneimine *N*-oxide **233**.



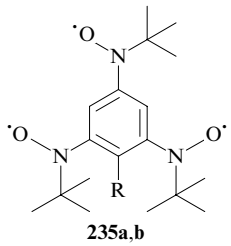
15a **233**

N,*N*′-Biphenyl-3,5-diyldi(*tert*-butyl nitroxide) **234** is more stable. This made it possible to study the molecular and crystal structure of biradical **234** and provided an interpretation for its diamagnetic behaviour in the solid phase in the temperature range of 1.8–300 K. It was found that in solid **234**, the intermolecular distances between the oxygen atoms of the N∴O groups are equal to 2.321(2) and 2.359(2) Å, which is much shorter than the sum of their van der Waals radii and the N∴O bond lengths [1.303(2) and 1.294(2) Å] are longer than the typical N∴O bond lengths in other *tert*-butylphenyl nitroxides. This means that in the crystal of **234**, a weak bond is formed between the N∴O groups, the bond energy being characterized by the antiferromagnetic exchange $2J/k \approx -1700$ K.[252]

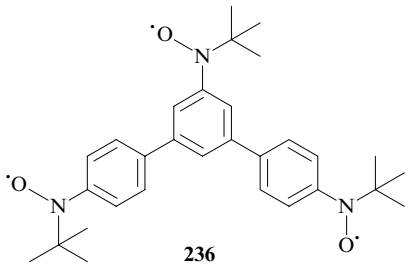


234

Due to the increase in the stability of poly(*tert*-butyl nitroxides) caused by introduction of substituents in position 5 of the 1,3-phenylene system, triradicals **16**, **235a** and **236** were isolated.[74,75] Trinitroxide **16** is a linear three-spin cluster characterized by $J/k = 240$ K. Strong ferromagnetic type exchange interaction ($J/k \approx 200-500$ K) also occurs in the triangular spin cluster **235a**. In the exchange cluster of NR **236**, the type of exchange interaction is retained but owing to the extension of the π-system connecting the paramagnetic centres, the J/k value decreases to 5.3 K. The replacement of the central 1,3,5-benzenetriyl fragment in **236** by a triazine fragment increases J/k to 15.3 K upon a decrease in the dihedral angles between the planes of the benzene rings and the plane of the triazine ring and a decrease in the torsion angles between the NO groups and phenyl rings.[253] The exchange interaction energy in the clusters with the 1,3-phenylene fragment decreases following an increase in the dihedral angle between the $C_{Ph}-N\therefore O$ plane and the phenyl ring plane caused by introduction of a substituent into position 2 of the phenyl ring (between two *tert*-butyl nitroxide groups). One can make sure of this by comparing the magnetic properties of radicals **235a** and **235b** (the exchange cluster in **235b** is an isosceles triangle with $J_1/k \approx 68.4$ K and $J_2/k \approx 5.0$ K).



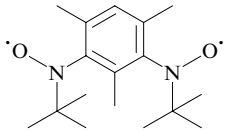
235a,**b**



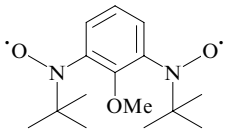
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R = H (**a**), OMe (**b**).

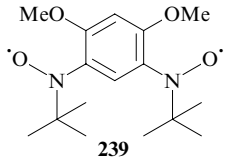
This example shows that the type of exchange interaction depends appreciably on the mutual orientation of the magnetic orbitals. Deviations from the parallel orientation caused by conformational distortions of the structure can entail a decrease in the exchange interaction energy and change in the sign.[254] Indeed, nitroxides **237**–**239** have a singlet ground state.[255] According to X-ray diffraction data, the presence of 4- and 6-MeO groups in the 1,3-phenylene fragment of biradical **239** induces a *syn*-rotation of the planes of nitroxide groups ($C_{Ph}-N\therefore O$) relative to the phenyl ring plane through dihedral angles of 65.1° and 75.3°, respectively. The singlet–triplet splitting is characterized by $2J/k = -74$ K. It is curious that in the solid solution of biradical **239** in poly(vinyl chloride) (~2 mol %), the value of $2J/k$ parameter decreases to −7.0 K, which is due to a change in the molecular conformation.[256] It is noteworthy that after fast cooling of a solution of biradical **240** in 2-methyltetrahydrofuran from ambient temperature to 5 K the singlet state is retained, but on further keeping at low temperature, the singlet state is replaced by the triplet ground state.[257]



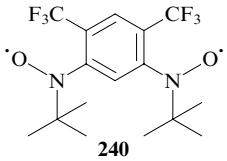
237



238

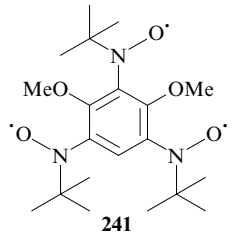


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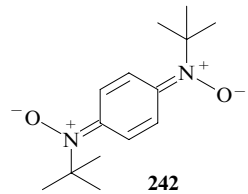
240

In biradical molecules **238** and **239**, the energy of intramolecular exchange interaction of unpaired electrons is antiferromagnetic and differs by an order of magnitude on going from one compound to another. These data served as the basis for the targeted synthesis of triradical **241**. According to X-ray diffraction data, in triradical **241** all paramagnetic substituents occur in the *syn*-conformation; the $C_{Ph}-N\therefore O$ planes of the equivalent N∴O groups form a dihedral angle of 90° with the plane of the phenyl ring and the $C_{Ph}-N\therefore O$ plane of the remaining nitroxide group forms an angle of 79°. This geometry of compound **241** favours the competing antiferromagnetic exchange interactions, therefore, the ground state of triradical **241** is a doublet.[258]



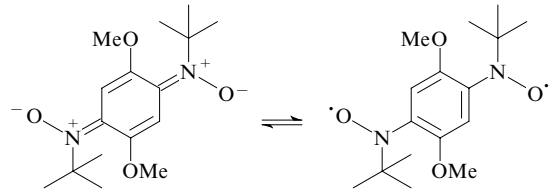
241

In relation to the studies of the effect of mutual orientation of magnetic orbitals on the type of exchange interaction, the magnetic-structural relationships inherent in di(*tert*-butyl nitroxides) containing a classical antiferromagnetic binding 1,4-phenylene fragment deserve attention. Unsubstituted *N*,*N*′-1,4-phenylenedi(*tert*-butyl nitroxide) exists in solution and in the solid phase only in the quinonoid form **242**.



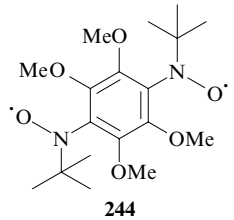
242

2,5-Dimethoxy derivative **243** also acquires a quinonoid form in the solid state but in solution, it exists as equilibrium of two tautomers **243a** and **243b**.



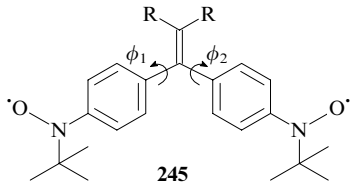
243a **243b**

Tetramethoxy-1,4-phenylene dinitroxide **244** exists at room temperature only in the biradical form. In the solid phase, the nitroxide groups of **244** occur in the *anti*-conformation, the planes $C_{Ph}-N\dot{-}O$ form a dihedral angle of 84.5° with the plane of the phenyl ring. According to magnetochemical measurements, the intramolecular exchange interaction parameter is $2J/k = -3.6$ K.[259]



244

Another group of polynitroxides, $O\dot{-}N-A^n(N\dot{-}O)_x$, is represented by compounds in which the binding fragment follows a trimethylenemethane topology. The proper trimethylenemethane has a low-lying triplet ground state;[260, 261] however, in its topological heteroatomic invariants, bis(nitroxides) **245**,[262–264] the amplitude and the sign of the exchange interaction depend appreciably on the torsion angle (ϕ) between the aromatic rings and the ethylene bridge.



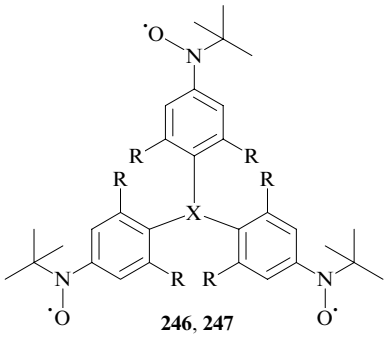
245

Thus analysis of magnetic-structure relationships inherent in bis(nitroxides) **245** has shown that the intramolecular exchange parameter (J) can be estimated from the equation

$$J\,(\mathrm{cm}^{-1}) = 44\cos^2\bar{\phi} - 17,$$

where $\bar{\phi} = (\phi_1 + \phi_2)/2$ is the average value of the torsion angle. According to this equation, the maximum J value for bis(nitroxides) **245** is 27 cm^{-1}; hence, the spin density on the carbon atoms bound to the ethene fragment is ~0.1.[263]

The replacement of the ethene fragment by quinonoid electron-withdrawing groups proved to be essential for increasing the energy of ferromagnetic interaction in trimethylenemethane nitroxide invariants. Thus the $2J/k$ value increases to 410 K on going from compound **245** to biradical **17**, which exists in the solid phase as a superposition of two canonical forms **17a** and **17b**, as was indicated by X-ray diffraction data.[87, 88] The change in the number of π-electrons in analogues of **17** upon replacement of the central C atom by the N or B atom changes the type of exchange interaction from ferromagnetic to antiferromagnetic. Therefore, the ground state of molecules **246** and **247** is doublet and lies 559 and 10 K, respectively, lower than the quartet state.[87, 265]



246, **247**

246: X = N, R = H; **247**: X = B, R = Me.

The removal of two phenyl rings in compound **17** does not result in the expected increase in the energy of intramolecular exchange interaction (ΔE_{T-S}): indeed, in bis(nitroxide) **227**,[248] the triplet ground state is lower by 319 K than the singlet state.[266] This may be due to low contribution of the quinonoid structure **227b**, as indicated by the great angle between the plane of the ONCNO fragment and the plane of the Ph ring (~22°) and to slight alternation of bond lengths in the benzene ring (C–C bond lengths in the ring differ by only 0.02 Å). In the solid phase of biradical **227**, the intermolecular antiferromagnetic exchange interactions ($2J/k = -14.5$ K) form 1D-systems (Fig 9). At temperature below $T_N = 1.1$ K, a magnetic phase transition takes place.[267]

Thus, the sign and the magnitude of the exchange energy in the phenylogues of polyazotrimethylenemethane are largely determined by the contribution of the quinonoid structure and the magnitude of the spin density on atoms connected to the ethene fragment. The latter, in turn,

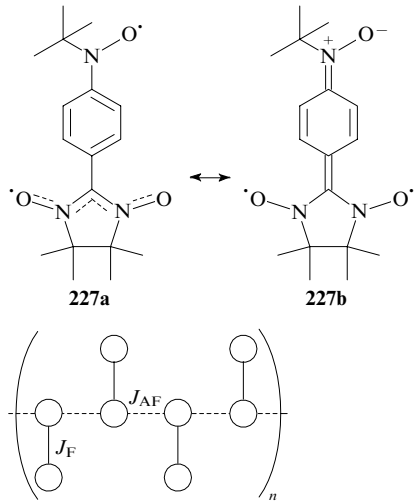
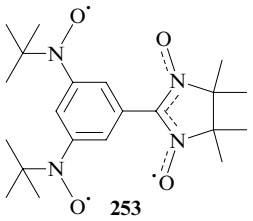


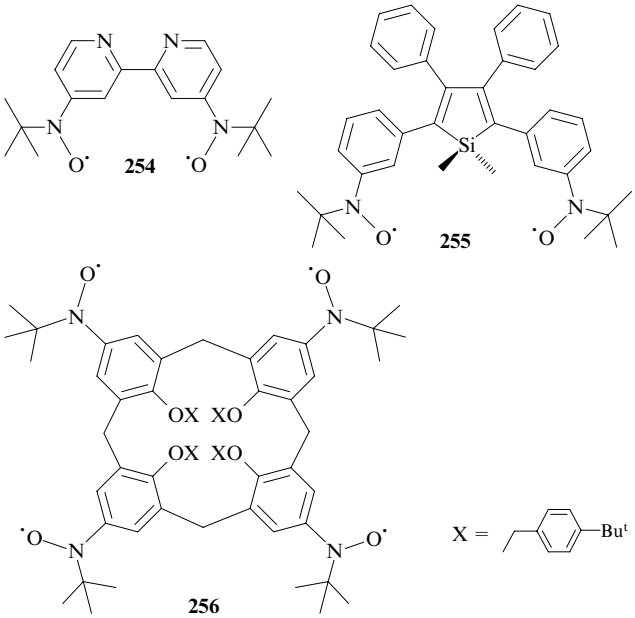
Figure 9. 1D-Chains in solid **227**.

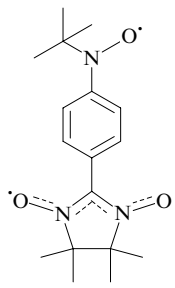
depend on the geometry and the electronic structure of the molecule. The effect of structural changes on the ferromagnetic exchange parameter is shown below for transition from biradical **227** to difluoro derivative **248**, imino nitroxide biradical **249**,[267] 4,4′-biphenylene biradical **250**[268] and triradicals **25**, **26** and **251**.[105] On going from *para*-isomer **227** to the *meta*-isomer **252** the sign of the parameter J/k changes.[269]

The found trends were used in planning the structure and synthesis of triradical **253**. According to magnetochemical measurements, exchange interactions of the opposite sign occur in this triradical: $J_F/k \sim 430$ K, $J_{AF}/sk = -108$ K; at low temperatures this predetermines the behaviour of the solid phase of the compound as a system formed by two types of paramagnetic centres with the spins $^1/_2$ and 1. At a temperature below 0.28 K, ferrimagnetic 3D ordering of structure **253** takes place as a result of weaker ($J'/k = -0.3$ K) intermolecular antiferromagnetic exchange interactions.[269]

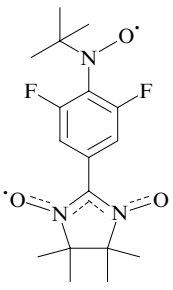


Several examples of polynitroxides with more complex bridging groups are presented below. Biradical **254** specially synthesized for the assembly of hetero-three-spin three-centre cluster tends to undergo intramolecular antiferromagnetic exchange with $J/k = -19$ K.[270] Biradical **255** containing a luminescent fragment has a singlet ground

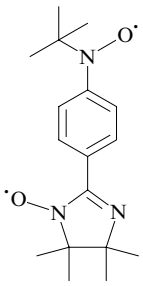




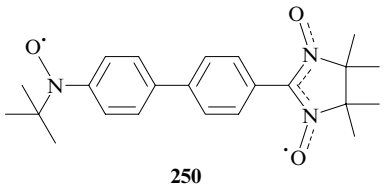
227
$J/k = 319$ K



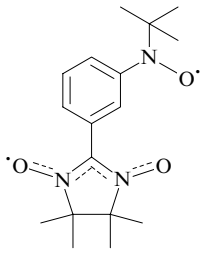
248
$J/k = 204$ K



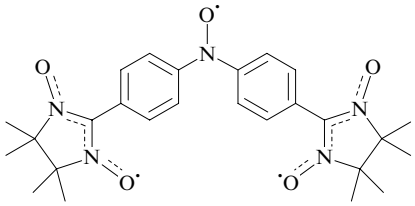
249 ($T_N = 2.5$ K)
$J/k = 108$ K



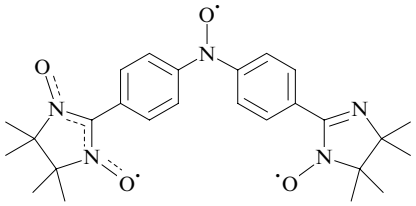
250
$J/k = 72$ K



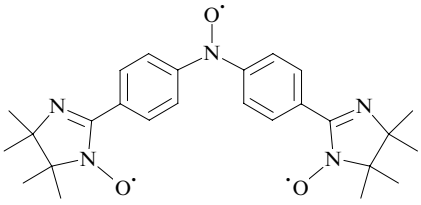
252
$J/K = -68$ K



26
$J/k = 231$ K



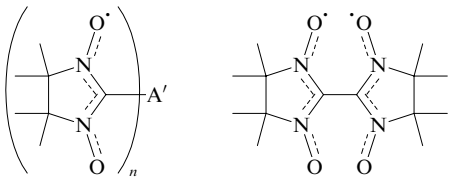
25
$J_{12}/k = 319$ K,
$J_{23}/k = 130$ K



251
$J/k = 130$ K

state ($J/k = -6$ K).[271] In the solid phase of tetranitroxide **256**, a calix[4]arene functionalized at the upper rim by four *N*-*tert*-butyl-*N*-oxyl-amino groups, one diagonal nitroxide pair is dimerized, which imparts a pinched cone conformation to this tetraradical and induces strong antiferromagnetic exchange interactions with $|J/k| = 200-300$ K.[272]

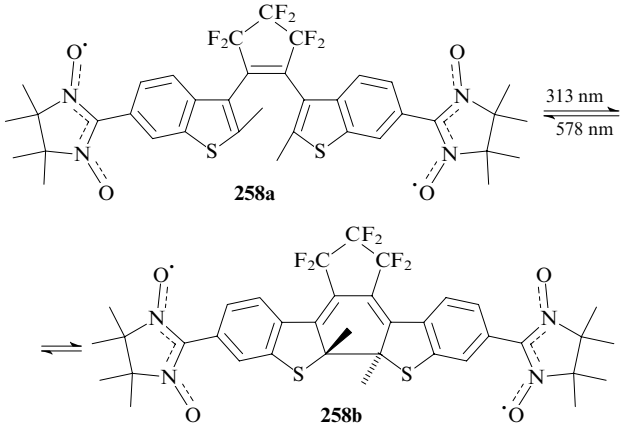
π-Bonding of paramagnetic fragments in two 2-imidazolin-1-oxyl 3-oxides furnishes a number of biradicals **257**, which starts with biradical **257a**.



257 **257a**

In solid biradical **257a**, the paramagnetic fragments are rotated relative to each other by 55°. Therefore, the energy of intramolecular exchange interaction in biradical **257a** ($2J/k = -216$ K)[§] is smaller in absolute magnitude than in biradical **257b** with ethylene bridge in which the ONCNO and $-CH=CH-$ fragments lie in one plane (Table 6). On further increase in the number of unsaturated fragments in the A′ bridge, the splitting between the triplet state and the ground singlet state decreases. If the A′ bridge is a *m*-phenylene fragment, then, as discussed above, the intramolecular exchange interaction becomes ferromagnetic. The depth of the triplet state decreases upon increase in the angle α and on going to the vinylogues or phenylogues including their heteroatomic analogues.[273]

Biradicals with a photoswitchable exchange channel A′ were synthesized. For example, in biradical **258a**, 1,2-bis(2-methylbenzo[*b*]thiophen-3-yl)perfluorocyclopentene fragment A′ cyclizes in solution on exposure to UV radiation at $\lambda = 313$ nm, while on exposure to light at $\lambda = 578$ nm, recyclization occurs, the conversion in both forward and back photoreactions being about 100%. According to magnetochemical measurements, upon the photochemical cyclization of the diarylethene fragment A′, the intramolecular antiferromagnetic interaction between the unpaired electrons increases from $2J/k = -2.2$ K to $2J/k = -11.6$ K [for a 3% solution of **258b** in poly(*n*-butyl methacrylate), $2J/k = -12.5$ K].[287,288]

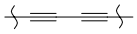
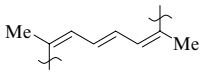
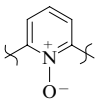
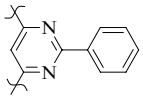
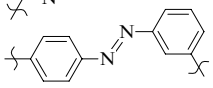
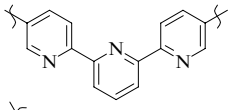
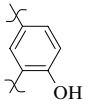


258a

258b

§ In solution, this parameter varies insignificantly: $2J/k = -203$ K, indicating that the gauche conformation is retained upon dissolution of **257a**.

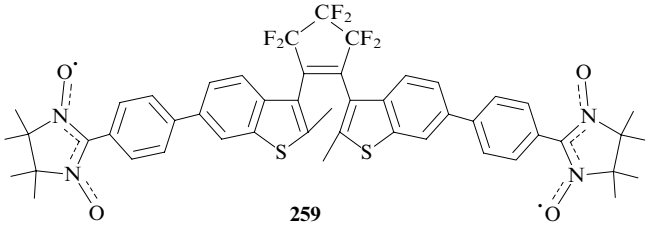
Table 6. Magnetic-structure correlations for compounds **257**.

Fragment A′	α /deg [a]	$2J/k$ /K	Ref.
None	55	−216 [b]	274
	0	−460	152, 275
		−207	see [c]
	25	−90 −95	152 276
	31	−75	276
	90, 57	−3.6	277
	21, 28	1.7	278
	33, 34	8.4	279
	30, 32	15	280
	40, 36	26	281
	36, 32	∼20 ∼0 46 72 ± 20 [d]	282 283 284 285
	33, 26	23 [e]	286

[a] Angle between the ONCNO plane and the substituent plane. [b] Dimer model. [c] Our data. [d] Found from the dependence of the magnetic susceptibility $\chi_{EPR}(T)$ of a solution of the biradical in polystyrene. [e] The data were obtained for mixed 1 : 1 crystals of the triradical with 1,3,5-trinitrobenzene.

In biradicals **258a** and **258b**, the exchange interaction between the unpaired electrons is much greater than the HFC constant; therefore, their EPR spectra are identical.

In biradical **259**, the presence of two additional *p*-phenylene groups in the bridging A′ fragment decreases the $2J/k$ value to 10^{-3} K ($2J/g\mu_B \approx 0.8$ mT), which is comparable with the HFC constant. The photochemical cyclization of biradical **259** sharply increases the exchange interaction between the unpaired electrons and the $2J/k$ value becomes greater than 0.08 K ($2J/g\mu_B >$ 60 mT $\gg a_N$). This enables detection of photocyclization of biradical **259** and photorecyclization in solution, *i.e.*,

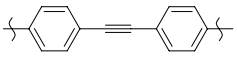
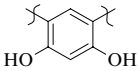


259

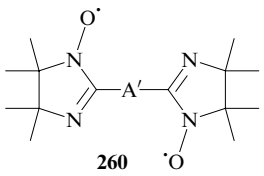
compound **259** can thus be used as EPR-controlled photomagnetic probe.

In the series of π-bonded 2-imidazolin-1-oxyls **260**, the most closely spaced paramagnetic fragments are found in biradical **260a**. In solid **260a**, the paramagnetic fragments are rotated relative to each other through 54°, *i.e.*, virtually through the same angle as in **257a**. The intramolecular exchange interactions in compound **260** are antiferromagnetic, $2J/k = -194\ cm^{-1}$. In solution, this parameter changes insignificantly ($2J/k = -163\ cm^{-1}$), which attests to retention of the biradical form upon dissolution.[274] We will not discuss the effect of the structure of the A′ fragment on the energy and sign of intramolecular exchange interactions in the series of compounds **260** (the relevant data are briefly summarized in Table 7, because the key conclusions would be the same as made for the series of compounds **257** (see Table 6).

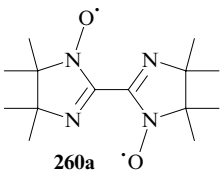
Table 7. Magnetic-structure correlations for compounds **260**.

Fragment A′	α /deg [a]	2J/k /K	Ref.
None	54	−194 [b]	274
	—	−9.7 [c]	273
	8.7, 4.9	10 [d]	289
	57.8, 52.9	7 ± 2.5 [e]	290
	37, 34	20 ± 10 [c]	285
	37, 4	50 ± 2 [d]	285
		40 ± 2 [d]	291

[a] Dihedral angle between the NCNO plane and the substituent plane. [b] Dimer model. [c] Found from the dependence of the magnetic susceptibility $\chi_{EPR}(T)$ of a solution of the biradical in polystyrene. [d] Four-spin cluster model. [e] Found for a solid solution of the biradical in PVC.



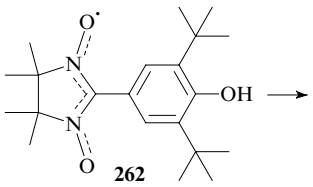
260



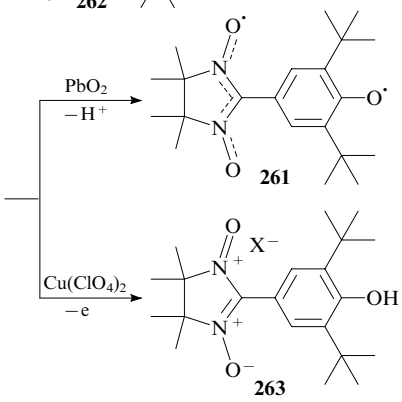
260a

6. Heterobiradicals $O \div N - A^nR^{\bullet}$

π-Bonding of the 1-oxyl-3-oxide-imidazolin-2-yl group to radical fragments of a different type gives rise to heterobiradicals, which are now fairly exotic (heteropolyradicals have not been reported as yet). Of particular interest among these biradicals are stable heteroatomic analogues of trimethylenemethane, as they may possess a triplet ground state. For example, this is paramagnetic compound **261**, which was prepared in a quantitative yield by oxidation of radical **262**.[292,293] It is of interest that oxidation of radical **262** either electrochemically or on treatment with $Cu(ClO_4)_2$ in MeCN yields oxoammonium salt **263**, which is also formed on the addition of CF_3CO_2H to biradical **261**. (Similar salts are formed in NR disproportionation processes.) The addition of pyridine to salt **263** induces the reverse transformation.



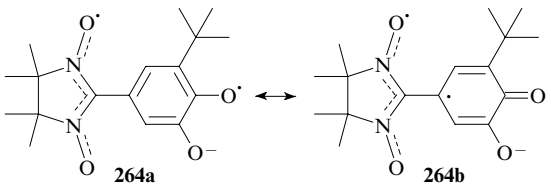
262



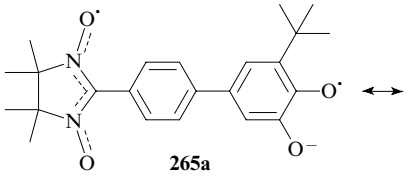
261

263

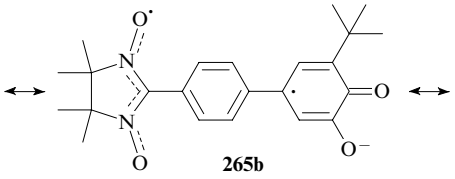
Biradical anions **264** and **265** were isolated and described as coordination compounds with metals. The *o*-semiquinone ring is bound to the 3-oxide-1-oxoimidazolin-2-yl group by the π-bridge, giving rise to a quinoid distortion of the *o*-semiquinone system (X-ray diffraction data). In both anions, strong ferromagnetic type exchange interaction takes place ($> 300\ cm^{-1}$ in **264** and $> 100\ cm^{-1}$ in **265**) as a result of covalent bonding of the substituent C atom (with positive spin density) to the C(2) atom of the imidazoline ring with negative spin density.[294–296]



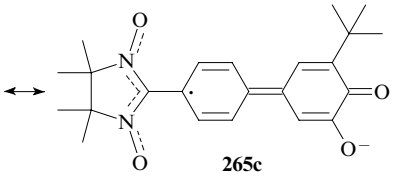
264a **264b**



265a



265b

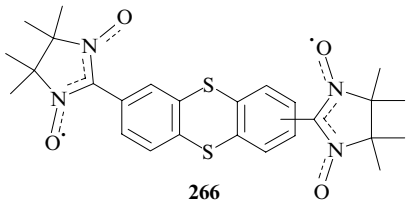


265c

Apart from the compounds considered above, which exist initially as heterospin biradicals, there is a group of compounds that combine in one molecule a paramagnetic fragment and a group with high-lying HOMO conjugated with this fragment. Single-electron oxidation of such compounds may afford multispin exchange clusters.[172] For

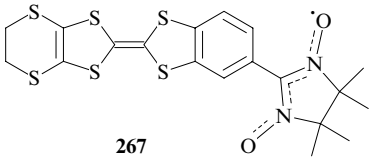
example, single-electron oxidation of radical **134b** with iodine in THF gave a biradical cation with $|D|$ and $|E|$ parameters of 0.0276 and 0.0016 cm^{-1}, respectively. The reaction of **134b** with DDQ furnished complex **134b**·DDQ with only one unpaired electron per molecule, as shown by magnetochemical measurements. In the authors' opinion, the fragments **134b**·DDQ are three-electron systems with strong antiferromagnetic interaction of two unpaired electrons.[168]

The growing demand for organic multispin systems able to serve as operating components in conducting electronic devices stimulated the synthesis and study of a specific group of NR.[297, 298] It was shown that single-electron oxidation of isomeric 2,7- and 2,8-biradicals **266** yields in both cases triradical cations with a quartet ground state.[299]

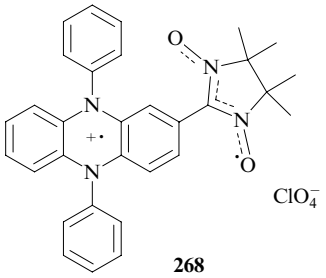


266

The galvanostatic electrocrystallization of compound **267** from a trichloroethylene (TCE)–THF mixture produced a radical ion salt $[\mathbf{267}]_2ClO_4[TCE]_{0.5}$,[300] and the oxidation of spin-labelled 5,10-diphenyl-5,10-dihydrophenazine with tris(4-bromophenyl)ammonium perchlorate in MeCN afforded salt **268** in the multispin cation of which strong intramolecular exchange takes place ($2J/k \geqslant 700$ K).[301]



267



268

IV. Conclusion

The active use of polyfunctional stable NR as building blocks for magnetically active compounds has promoted a considerable progress in the design of these compounds. An exceptionally valuable feature of these NR is the simultaneous presence in their molecules of fragments with efficiently delocalized spin density and donor fragments capable of coordination to metal ions. On bridging coordination of NR to paramagnetic metal ions, the donor groups in the NR can be arranged in a definite way, which predetermines the spatial topology of the molecular magnet thus formed.

Methods for the synthesis of NR with delocalized spin density that can bear a negative charge have been developed. When coordinated by a metal ion, these ligands counterbalance the positive charge of the metal ion, and this makes it possible to get rid of the useless diamagnetic anions in the resulting multispin compound. New approaches to the synthesis of conjugated stable NR containing heteroatomic groups at the α-carbon atoms were developed.[144, 302, 303] Unsaturated nitroxides, which have been long classified as unstable radicals that cannot be isolated, were synthesized.

Nitroxide radicals able to undergo transition to the magnetically ordered state were prepared. All the known purely organic paramagnets of this type are ordered at low temperature. However, the mere fact of the possibility of ordering stimulates the researchers to design new NR able to undergo bulk magnetic ordering at high temperature. Note that the heterospin $Cu(hfac)_2$ complexes with NR served as the basis for the design of unusual 'breathing' crystals the spin transitions in which cause a giant reversible thermostriction effect.

It can be seen from the material presented in this review that the methods for NR synthesis are permanently advanced. In many cases, it is possible to perform targeted synthesis of NR needed for the construction of novel magnetically active compounds with specified structure and magnetic properties. We have already noted in the Introduction that data on the chemical design of polyfunctional stable NR needed for the development of research in the design of molecular magnets appear in journals devoted to diverse subject matters. It cannot be ruled out that this would require the search for special forms for generalizing the accumulated knowledge. We hope that the material considered in this review would be useful not only for chemists but also for researchers working in the fields of physics, physical chemistry, material science, biology, biochemistry and medicine.

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